



9th International Conference on Carbonaceous Particles in the Atmosphere

12-14 August 2008

**Lawrence Berkeley National Laboratory
Berkeley, California**



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California Environmental Protection Agency





9th International Conference on Carbonaceous Particles in the Atmosphere

August 12-14, 2008

Lawrence Berkeley National Laboratory, Berkeley, California

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Proceedings Publication

A. Strawa, Moffit Field



Thirty Years of Carbon Conferences

Year and Venue	Proceedings
1978 Berkeley	Lawrence Berkeley National Laboratory, Report #LBL-9037, 1979
1983 Linz	The Science of Total Environment, Vol. 36, 1984
1987 Berkeley	Aerosol Sci and Technol. Vol. 10, No. 1&2, 1989; Vol. 12, No. 1, 1990
1991 Vienna	Atmospheric Environment, Vol. 27A, No.8, 1993
1994 Berkeley	Journal of Geophysical Research, Vol. 101, D14, 1996
1997 Vienna	Atmospheric Environment, Vol. 33, No. 17, 1999
2000 San Juan	Journal of Geophysical Research, Vol. 107, D21, 2002
2004 Vienna	Atmospheric Chemistry and Physics, Special Issue 2005
2008 Berkeley	TBD

9th Conference Citizenship of 147 Participants (as of 1-Aug 2008)

Country	No.	(%)	Country	No.	(%)
United States	71	48%	Canada	2	1%
India	9	6%	Czech Republic	2	1%
Japan	7	5%	New Zealand	2	1%
Austria	5	3%	Bangladesh	1	1%
Germany	5	3%	Greece	1	1%
Italy	5	3%	Hong Kong	1	1%
China	4	3%	Iran	1	1%
Sweden	4	3%	Ireland	1	1%
Finland	3	2%	Kenya	1	1%
France	3	2%	Korea	1	1%
Hungary	3	2%	Portugal	1	1%
South Korea	3	2%	Russia	1	1%
Spain	3	2%	Slovenia	1	1%
Australia	2	1%	Switzerland	1	1%
Belgium	2	1%	United Kingdom	1	1%

PROGRAM

MONDAY 11-Aug 2008

1800-2100 Welcome gathering, badge and material pick-up & reception at Doubletree hotel

TUESDAY 12-AUG 2008

0800 Shuttle service from Doubletree to LBNL Bldg 50 auditorium

0830 On-site check-in (30 min)

Welcome

0900 Kirchstetter, T – Conference Co-Chair

0915 Steve Chu, Director of LBNL

Black Carbon Historical Trends (Session Chairs: T. Bond and G. Ban-Weiss)

(Refreshments served)

0930 McConnell, J – Historical black carbon concentrations and deposition rates from ice cores

0950 Husain, L – Trends in atmospheric elemental carbon concentrations from 1835 to 2007

1010 Kaspari, S – Carbonaceous particle concentrations since the pre-industrial era from Asian ice cores

1030 Guillaume, B – Global emission inventories of gases and particles from fossil fuel and biofuel consumption for the period 1860-2030 with tentative validations with carbonaceous aerosol TM4 global modeling

1050 Break (20 min)

Biogenic and Marine Aerosol (Session Chairs: M. Claeys and W. Maenhaut)

1110 Facchini, M – Discerning primary and secondary organics in marine aerosol particles

1130 Sciare, J – A biogenic marine source of organic aerosols: from field measurements in the Austral Ocean to model estimates of its contribution at a global scale

1150 Surratt, J – Organosulfate formation in biogenic secondary organic aerosol

1210 Bauer, H – Three Cities' Study of biogenic emissions: annual trend and contribution of wood smoke and fungal spores to organic carbon in PM10 aerosols in Austria

1230 Lunch break (70 min)

Secondary Organic Aerosol (Session Chairs: U. Baltensperger and S. Decesari)

(Refreshments served)

1340 Baltensperger, U – Secondary organic aerosol formation in a smog chamber and its link to source apportionment in the real atmosphere

1400 Bhawe, P – Simulating secondary organic aerosol across the United States – sensitivity analyses using the CMAQ model

- 1420 Jonsson, Å – Influence of temperature and water on secondary organic aerosol formation from the ozonolysis of limonene, Δ^3 -carene and α -pinene
- 1440 McFiggans, G – Composition and properties of aerosol formed in the photo-oxidation of a Range of terpenes at atmospherically reasonable concentrations in a heavily instrumented simulation chamber
- 1500 Smith, J – OH Oxidation of organic aerosols

1520 Break (30 min, **time to put up your poster in the cafeteria**)

OC & BC Analytical Techniques I (*Session Chairs: R. Chakrabarty and T. Kirchstetter*)

- 1550 Onasch, T – A new instrument for measuring the mass, size, and chemical composition of soot containing particles
- 1610 Hill, S – Single-particle Laser-Induced Fluorescence (LIF) spectra of atmospheric aerosol: effects of brief heating
- 1630 Hering, S – An in-situ method of organic aerosol speciation via thermal desorption gas chromatography-mass spectrometry (TAG)
- 1650 Hitzenberger, R – Measurements of black and brown carbon in atmospheric aerosols with the integrating sphere method
- 1710 Cappa, C – Bias in filter based aerosol absorption measurements due to organic aerosol loading: evidence from laboratory and field measurements

1730 End of day 1 oral presentations, walk to poster session in cafeteria

Poster Session (*Refreshments served*)

- 1745 Poster session starts
- 2045 Poster session ends
- 2100 Shuttle service from LBNL to Doubletree

WEDNESDAY 13-AUG 2008

- 0800 Shuttle service from Doubletree to LBNL bldg 50 auditorium
- 0830 On-site check-in, Open technical discussion (30 min)

Historical Overview: 30 Years of ICCPA

- 0900 Puxbaum, H – Conference Co-Chair

California's Perspective

- 0925 Ayala, A – Assessment of carbonaceous aerosols for California's Climate Protection Plan

Aging and Transformation (*Session Chairs: A. Williamson and A. Ayala*)

(*Refreshments served*)

- 0945 Riemer, N – Modeling soot aging with a stochastic particle-resolved aerosol model
- 1005 Gilles, M – Black carbons, fresh, and aged biomass burn particulates: evidence of oxygenated interfaces

1025 Break (20 min)

Ambient Concentrations (*Session Chairs: A. Williamson and A. Ayala*)

- 1045** Sciare, J – Factors influencing urban carbonaceous aerosols: comparison of Beijing (RP China), Paris (France), Cairo (Egypt) and Ouagadougou (Burkina Fasso)
- 1105** Jia, Y – Comparison of sugar composition in fine particulate matter at four sites in eastern Texas and central Arizona
- 1125** Rogge, W – Seasonal variations of highly time-resolved organic compounds concentrations of primary and secondary nature during the Baltimore PM_{2.5}-Supersite Study
- 1145** Kim, Y – Characteristics of carbonaceous aerosol in Guangzhou during the 2006 PRD campaign: optical properties and mixing state

1205 Lunch break (85 min)

OC & BC Analytical Techniques II (*Session Chairs: R. Cary and A. Gelencsér*)

(*Refreshments served*)

- 1330** Cavalli, F – Toward a standardized thermal-optical protocol for measuring atmospheric organic and elemental carbon: the Eusaar Protocol
- 1350** Wallén, A – Charring characteristics of water-soluble organic carbon from samples with diesel exhaust fume and wood smoke analyzed by a thermo-optical transmittance method
- 1410** White, W – Relating OC/EC data from two national monitoring networks
- 1430** Hadley, O – Thermal Spectral Analysis
- 1450** Subramanian, R – Towards a reference material for soot measurement: evaluation of candidates with scanning electron microscopy, an SP2, a Pass and an OC/EC analyzer

1510 Break (20 min)

Isotopic Analytical Techniques (*Session Chairs: M. Gilles and N. Perron*)

- 1530** Ruehl, C – Stable isotope ratios of water soluble organic aerosols separated by size exclusion chromatography
- 1550** Szidat, S – Refined ¹⁴C source apportionment of organic carbon
- 1610** Kundu, S – Stable carbon and nitrogen isotopic composition of biomass burning aerosols and their molecular composition of diacids and related compounds: LBA-SMOCC campaign from Rondônia, Brazil

1630 End of day 2 oral presentations

1645 Shuttle service from LBNL to Doubletree

Dinner Cruise in SF Bay

1745 Board Hornblower yacht for dinner cruise behind Doubletree hotel

2100 Hornblower dinner cruise ends

THURSDAY 14-AUG 2008

0800 Shuttle service from Doubletree to LBNL bldg 50 auditorium

0830 On-site check-in (30 min)

Keynote (*Session Chair: T. Novakov*)

0900 Ramanathan, V – Black carbon: A major issue for mitigating global and regional climate

Optical Properties (*Session Chairs: R. Bergstrom and A. Strawa*)

(*Refreshments served*)

0950 Litton, C - Optical properties of multi-component mixtures of carbonaceous dusts and aerosols

1010 Chakrabarty, R – Morphology and effective refractive indices of aerosols emitted from high moisture content biomass combustion

1030 Chen, Y – Light absorption by organic carbon from wood combustion

1050 Break (20 min)

Biomass and HULIS (*Session Chairs: C. Baduel and L. Iraci*)

1110 Schmidl, C – Chemical characterization of wood smoke particle emissions and its application to source apportionment

1130 Mayol-Bracero, O – Black carbon and organic carbon during SMOCC: the absorbing fraction of biomass burning aerosols in the Amazon basin

1150 McMeeking, G – Characterization of emissions from the laboratory combustion of wildland plant species

1210 Yu, Jian Z – Size distributions of HULIS in fresh biomass burning aerosols and ambient aerosols in south China

1230 Lunch break (90 min)

Effects on Regional and Global Climate (*Session Chairs: A. Clarke and S. Menon*)

(*Refreshments served*)

1400 Clarke, A – Combustion aerosol as a source of CCN on global scales: Amazon biomass burning and other continental sources

1420 Hansson, H – Changing natural-anthropogenic aerosol mixture over northern Europe and its possible effect on regional climate

1440 Jacobson, M – The differential global and regional climate and air-pollution health effects of fossil-fuel versus biofuel soot

1500 Vignati, E – Two sources of uncertainties in modeling black carbon at global scale

1520 Flanner, M – Snow-albedo feedback triggered by carbonaceous particles

1540 Break (20 min)

Organic/Inorganic Interactions (*Session Chairs: H. Puxbaum and M. Lunden*)

1600 Gelencsér, A – Bulk characterization of organosulfates in continental fine aerosol

1620 Ma, Y – Speciation of heterocyclic nitrogen compounds in biomass burning aerosols using two-dimensional gas chromatography-mass spectrometry with heart-cutting

1640 Silva, P – Secondary organic particle formation from reactions of amines with nitrate Radical

1700 Kiss, G – Joint effect of organic and inorganic aerosol components on cloud droplet activation

1720 End of day 3 oral presentations and conference

1800 Shuttle service from LBNL to Doubletree

POSTERS

Poster Session (1745-2045, Tuesday, 12 Aug 2008)		
No.	Presenter	Title
<i>Analytical techniques</i>		
1001	Adachi, Kouji	Internally Mixed Soot Particles From Mexico City: Individual-Particle Analysis Using Transmission Electron Microscopy
1002	Vander Wal, Randy L	Carbonaceous Aerosol: Physical Nanostructure and Chemical Analysis by XPS
1003	Chakrabarty, Rajan K	FracMAP: a Graphical User-Interactive Package for Performing Simulation and Orientation-Specific Morphological Analysis of Fractal-Like Aerosol Agglomerates
1004	Beránek, Josef	Optimization of Sensitive SPME Method for Analysis of Water soluble Aldehydes
1005	Bond, Tami	Revisiting thermal-optical analyses of carbonaceous aerosol using a physical model
1006	Ding, Luyi	Determination of Polycyclic Aromatic Hydrocarbons, N-Alkanes, Hopanes and Steranes in PM _{2.5} in Golden, Canada by Thermal Desorption GC-MS
1007	Ding, Luyi	Preliminary Results on Application of OC/EC Thermal Analyzer for the Analysis of Water Extractable Atmospheric Humic-Like Substances in PM _{2.5} Samples From Selected Sites in Canada
1008	Dillner, Ann M	Quantification of Organic Functional Groups and Inorganic Compounds in Ambient Aerosols and Determination of Sources Using Attenuated Total Reflectance FTIR Spectroscopy and Multivariate Chemometric Techniques at a Rural Site in Arizona
1009	Kubátová, Alena	Extractable Carbonaceous Particulate Matter and GC/MS Characterization of Polar Fraction
1010	Ranjan, Manish	A New Instrument for Near-Real Time Size-Resolved Organic Carbon Measurement
1011	Ma, Yilin	Direct Determination of Levoglucosan and Associated Species in Fine Particulate Matter With Thermal Extraction-GC-GC-MS

1012	Paredes-Miranda, Guadalupe	Photoacoustic and Aethalometer Measurements of Aerosol Light Absorption in the Presence of Secondary Organic Aerosol: Mexico City, Las Vegas & Reno Nevada, and the DOE ARM Site in Oklahoma
1013	Jennings, S. Gerard	Comparison of aerosol light absorption coefficient measurements at the Mace Head Atmospheric Research Station using a MAAP and an Aethalometer
1014	Tian, Guoxun	Calibration of Photoacoustic Aerosol Absorption Measurements With Oxygen A-Band Spectroscopy
1015	Fukushima, Nobuhiko	Newly Designed Black Carbon Monitor (Cosmos) and Its Performance
1016	Perron, Nolwenn	Optimized Separation of OC and EC for Radiocarbon-Based Source Apportionment of Carbonaceous Aerosol
1017	Castaneda, Carlos M	Use of Proton Backscattering to Determine the Carbon Content in Samples Deposited on Teflon Filters
1018	Chiari, Massimo	Analysis of Carbon in Aerosol Samples With Accelerated Proton Beams
1019	Fitz, Dennis R	Evaluation of PM _{2.5} Organic Carbon Sampling Artifacts: Comparison of Data From Impactors and Quartz Fiber Filters
1020	Maenhaut, Willy	Performance of a Diffusion Denuder for the Elimination of Sampling Artifacts for Carbonaceous Aerosols at Three Urban and Two Forested Sites in Europe
1021	Kirchstetter, Thomas	Got Milk? Making and Measuring Colloidal Suspensions of Black Carbon in Water
1022	Dillner, Ann	Effects of Post-Sampling Filter Treatments on the Measurement of Ambient Carbon Aerosols
1023	Jeremy Riggle for Chow, Judy	Assessment of Carbon Sampling Artifacts in the IMPROVE, STN/CSN, and SEARCH Networks

Optical properties

1101	Arnott, William P	Photoacoustic Evidence for Strong Spectral Variation of Biomass Smoke Light Absorption and Single Scattering Albedo
1102	Bergstrom, Robert W	Spectral Absorption by Atmospheric Carbonaceous Particles
1103	Kim, Hwajin	Measurement of Aerosol Refractive Index by Polar Nephelometer
1104	McMeeking, Gavin R	The Light Attenuation Spectral Dependence of Organic Carbon Emitted by Biomass Burning

- 1105 Eleftheriadis, K On The Dependence of Arctic Light Absorption Coefficient and Equivalent Black Carbon on Aerosol Origin and State of Mixing

Transport sector emissions

- 1201 Frey, Anna Size-Segregated Absorption Measurements of Traffic and Urban Background Aerosol
- 1202 Hasegawa, Shuichi Size-Resolved Carbonaceous Particles in Roadside and Ambient Atmosphere in Japan
- 1203 Ban-Weiss, George A Measurement of Black Carbon and Particle Number Emission Factors From Individual Heavy-Duty Trucks
- 1204 Lackey, Leila Particulate Emissions by a Small Non-Road Diesel Engine: (I) Biodiesel and Diesel Characterization and (II) Effect of Metal Salts and Sulfates on EGA Measurements
- 1205 Jakober, Chris Particulate Carbonyls From Gasoline and Diesel Motor Vehicles
- 1206 Mazurek, W Diesel Particulate Characterisation in the Maritime Environment
- 1207 Mazaheri, Mandana A new method for the remote characterization of aircraft engine emissions
- 1208 Mazaheri, Mandana Measurement of particle size distribution of commercial aircraft emissions
- 1209 Lee, Seung-Bok Comparison of Black Carbon Concentrations Among at Roadsides, on Roads, and in Roadway Tunnels
- 1210 Brown, Steven G Comparison of near-roadway carbon measurements in winter in Las Vegas

Source apportionment

- 1401 Dobovicnik, T Measurements of the Ratio of Aerosol Black Carbon (BC) to CO₂ in an Urban Basin as an Indicator of Dispersed-Source Combustion Efficiency
- 1402 Pio, Casimiro A Application of the Minimum OC/EC Ratio to the Source Apportionment of Organic Carbon in PM_{2.5} and PM₁₀ Aerosols: Evaluation of 15 Years of Measurements in Europe
- 1403 Tanner, Roger L Using Hourly OC/EC Ratios for Estimating Secondary Organic Aerosol Levels: Progress and Perils
- 1404 Hans-Christen Hansson for Krecl, Patricia Contribution of Residential Wood Combustion to Hourly Winter Aerosol in Northern Sweden Determined by Positive Matrix Factorization

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| 1405 | Minguillón, María-Cruz | Source Contributions to Fine and Quasi-Ultrafine Organic Carbon in the Los Angeles-Long Beach Harbor Area |
| 1406 | Zaveri, Rahul A | Contributions of Urban, Biomass Burning and Secondary Organic Aerosols Near Mexico City |
| 1407 | Saarikoski, Sanna | Sources of Fine Particle Organic Carbon in Helsinki Urban Air |

Modeling, transport and fate

- | | | |
|------|---------------------------|---|
| 2001 | Ilie, Marcel | Prediction of Particle Dispersion in Atmospheric Boundary Layer Using Large-Eddy Simulation |
| 2002 | Pio, Casimiro A | Particulate Carbon in Precipitation at European Rural/Background Sites |
| 2003 | Van Wyngarden, Annalise L | Kinetic Control of the Cloud Processing of Methylglyoxal in Aerosols: Implications for the Climate Forcing Properties of Organic Aerosols |
| 2004 | Vignati, Elisabetta | Modeling the Impact of Primary Insoluble Organics From the Sea |

Marine aerosols

- | | | |
|------|--------------------------|--|
| 2101 | Claeys, Magda | Evidence for Marine Production of Organosulfates from C9 - C11 Hydroxy Acids |
| 2102 | Facchini, Maria Cristina | Evaluation of the Wave-Breaking Zone Influence on Marine Aerosol Physico-Chemical Properties |

Secondary organic aerosol formation and mechanisms

- | | | |
|------|-----------------------|--|
| 2201 | Erupe, Mark E | Secondary Organic Aerosol Formation From Reactions of Tertiary Amines With Nitrate Radical |
| 2202 | Hennigan, Christopher | Enhanced SOA Formation Due to Water Uptake by Fine Particles |
| 2203 | Sciare, Jean | Water-Solubility and Volatility of Fresh Secondary Organic Aerosols |
| 2204 | Lunden, Melissa M | Bounding Analysis of Secondary Organic Aerosol Growth in the Vicinity of the Forest Canopy |
| 2205 | Iinuma, Yoshiteru | Identification of Cineole Oxidation Products in Biogenic Secondary Organic Aerosol |
| 2206 | Kahnt, Ariane | Particle and Gas Phase Analysis of Carbonyl Compounds Formed During Monoterpene Oxidation in Chamber Experiments |
| 2207 | Claeys, Magda | Characterization of Novel Tracers for α -/B-pinene Secondary Organic Aerosol |

2208	Claeys, Magda	Characterization of Organosulfates and Nitrooxy Organosulfates From the Photooxidation of Isoprene and Unsaturated Fatty Acids in Ambient Fine Aerosol
2209	Decesari, Stefano	Secondary Organic Aerosols From Anthropogenic Precursors: Bridging Field and Smog Chamber Observations
2210	Decesari, Stefano	Secondary Organic Aerosols From Biogenic Precursors: Bridging Field and Smog Chamber Observations

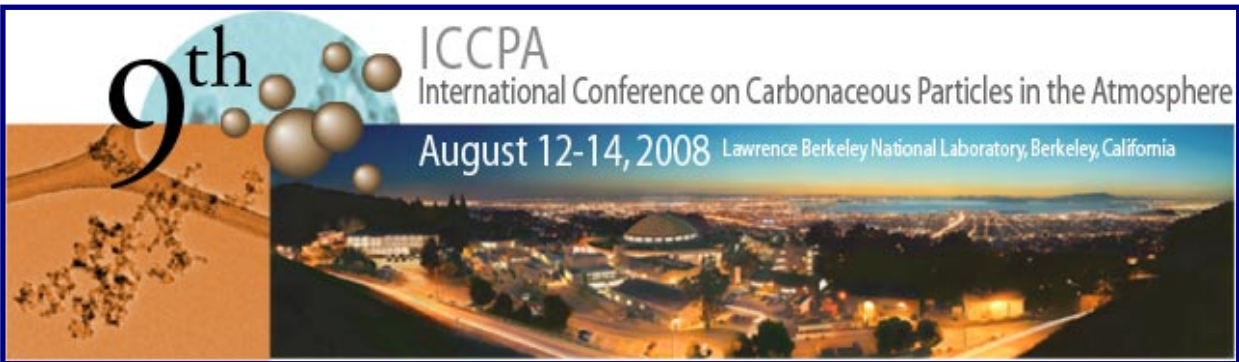
Ambient concentrations of carbonaceous particles

2301	Jankowski, Nicole	Seasonal and Local Variations of Carbonate Carbon in Ambient PM10 and Source Samples
2302	Sharma, Sangeeta	Spatial and Temporal Variations of Aerosol Optical and Chemical Properties at Five Canadian Sites
2303	Khan, A	Black Carbon in South Asian Megacities
2304	Ram, Kirpa	Carbonaceous Aerosols in Urban and High-Altitude Environment of North-India
2305	Maenhaut, Willy	Characterisation of Atmospheric Carbonaceous Aerosols in PM2.5 and PM10 Size Fractions at Two Sites in Tanzania
2306	Maenhaut, Willy	Mass Size Distribution of Organic Carbon and the Particulate Mass During a 2007 Summer Field Campaign at SMEAR II in Finland
2307	Maenhaut, Willy	Measurement of Carbonaceous Aerosols with a Semi-Continuous, Real-Time Carbon Aerosol Analysis Instrument at Three Forested Sites in Europe
2308	Maenhaut, Willy	One-Year Study of Organic and Elemental Carbon at Six Sites in Flanders, Belgium
2309	Maenhaut, Willy	Water-Soluble Organic Carbon in PM2.5 at Some Urban and Forested Sites in Europe
2310	Trompetter, Bill	Influence of environmental conditions on carbonaceous particle concentrations within New Zealand
2311	Davy, P.K.	Relationship between OC, EC and BC content of PM10 aerosol from a New Zealand urban airshed subject to air pollution events during winter
2312	Sánchez De La Campa, Ana M	Aerosol Carbonaceous Species Characterization in the South of Iberian Peninsula
2313	Samy, Shar	Water-Soluble Organic Compounds in Mid-Tropospheric Aerosols

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| 2314 | Hagino, Hiroyuki | A Case Analysis of Submicron Organic Aerosol Mass Spectra During Spring of 2008 at Tsukubain Japan |
| 2315 | Chiari, Massimo | Carbonaceous Components in PM10 in Tuscany (Italy): Results of a Year Long Campaign |
| 2316 | Edwards, Ross | Extreme Black Carbon Snow Concentrations from a Chinese Glacier |

Biomass and HULIS

- | | | |
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| 2401 | Baduel, Christine | Inter-Comparison of Two Methods for the Quantification of Humic Like Substances in Atmospheric Aerosol Particles |
| 2402 | Klatzer, Barbara | Humic-Like Substances in Airborne Particulate Matter: Seasonal Trends and Possible Sources |
| 2403 | Stone, Elizabeth A | Chemical Characterization of Humic Like Substances (HULIS) in North American Atmospheric Aerosols Using LC-MS/MS |
| 2404 | Stone, Elizabeth A | Source Apportionment of Carbonaceous Aerosol in the Kathmandu Valley: Sensitivity to Biomass Source Profiles |
| 2405 | Engling, Guenter | Characteristics of Organic Tracers for Biomass Burning on a Subtropical Island |
| 2406 | Iraci, Laura | Analyzing Biomass Burning Particle Composition With Infrared Spectroscopy |



ABSTRACTS

**Alphabetical Order in Presenter's
Name (as Listed in Program)**

**INTERNALLY MIXED SOOT PARTICLES FROM MEXICO CITY:
INDIVIDUAL-PARTICLE ANALYSIS USING TRANSMISSION ELECTRON
MICROSCOPY**

KOUJI ADACHI^{1,2} and Peter R. Buseck^{1,2}

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2. Department of Chemistry and Biochemistry, Arizona State University, Tempe, Arizona, USA

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Knowledge about the morphological properties and compositions of internal mixtures of soot (black carbon) particles with organic matter (OM) and sulfates is important. Climate models assume that aerosol particles are single phases (external mixtures), internal mixtures, or both. Internal mixtures are a better assumption if appropriate morphological and mixing properties are applied to the models, although these parameters are commonly not well known. Our goal is to understand their properties at the individual-particle scale. We used a transmission electron microscope (TEM) to analyze the morphologies, sizes, and compositions of internally mixed particles collected during the MILAGRO (Megacity Initiative: Local and Global Research Observations) campaign in and near Mexico City (MC) during March 2006. Soot is a common constituent of such mixtures, and the TEM can be used to recognize it based on its distinctive morphological features. We measured ~8000 particles (25 samples) with aerodynamic diameters from 0.05 to 0.3 μm . More than 50% of the particles consist of internally mixed soot, OM, and sulfate. Coatings on soot particles can amplify their light absorption. Coagulation with sulfates changes their hygroscopic properties, resulting in shorter lifetime. Our results suggest that a mixture of materials from multiple sources such as vehicles, power plants, and biomass burning occurs in individual particles, thereby increasing their complexity. Moreover, soot occurs in more than 60% of all particles in the MC plumes, suggesting its important role in the formation of secondary aerosol particles.

Reference

Adachi K and Buseck PR, Internally mixed soot, sulfates, and organic matter in aerosol particles from Mexico City, Atmospheric Chemistry and Physics Discussion, 2008.

PHOTOACOUSTIC EVIDENCE FOR STRONG SPECTRAL VARIATION OF BIOMASS SMOKE LIGHT ABSORPTION AND SINGLE SCATTERING ALBEDO

Kristin Lewis, WILLIAM P. ARNOTT, University of Nevada, Reno, Nevada, USA;
Hans Moosmüller, Desert Research Institute, Reno, Nevada, USA

Abstract

Simultaneous measurements of aerosol light absorption by a wide range of biomass smoke using the photoacoustic method at 405 nm and 870 nm are reported. Ångström coefficients for absorption were found to range from 1 to 3. These first of a kind measurements were made using a single photoacoustic instrument operating concurrently at two wavelengths. The measurements show that light absorbing organic material is present in wood smoke. Spectral properties of this organic material, which preferentially absorbs light at lower wavelengths, indicate that casual use of the inverse wavelength dependence of aerosol light absorption in remote sensing and modeling applications can introduce large errors in UV and visible wavelengths when compared with near IR absorption for certain types of wood smoke. Aethalometer measurement comparisons will be presented along with measurements by a photoacoustic instrument operating at a wavelength of 532 nm.

International Conference on Carbonaceous Particles in the Atmosphere
Lawrence Berkeley National Laboratory
August 12 – 14, 2008

ASSESSMENT OF CARBONACEOUS AEROSOLS FOR CALIFORNIA'S CLIMATE PROTECTION PLAN

Nehzat Motallebi, Dongmin Luo, and ALBERTO AYALA*
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PRESENTATION ABSTRACT

Atmospheric aerosols play an important role in the climate system through modifications of the global radiation budget: directly, by the scattering and absorption of radiation; indirectly, by the modification of cloud properties. The effect of aerosols on regional and global climate is extremely complex. A number of factors complicate the understanding of aerosol absorption, even at the local scale. The radiative properties of an individual particle are determined by composition, refractivity, size, and shape. There are considerable regional differences and uncertainties in the relationship between emissions and radiative forcing. Black carbon (BC), typically emitted as a fraction of PM from combustion processes, is the main light-absorbing component of aerosols. In recent years there has been increased attention to BC for global warming through direct effects, semi-direct effects, and changes in the albedo of ice and snow. The radiative properties of individual aerosol particles depend on the extent to which black carbon is mixed with primarily scattering aerosol components, such as sulfates and organics.

The California Global Warming Solutions Act of 2006 (AB 32) mandates reductions in emissions of the six greenhouse gases (GHG) included in the United Nation's Kyoto Protocol. AB 32 does not exclude consideration of other GHGs. Although remaining scientific uncertainties impede targeted climate policy action, the role of BC in climate change is an area of considerable interest. Public health is the overriding consideration for PM emission control, but it is recognized that reduction of BC emissions has definite climate benefits. However, quantifying the climate impacts of individual PM source types is not yet possible. Some scientists have reported that cleaning up diesels will conclusively provide an overall climate benefit. The same cannot be said about other BC sources – gasoline-fueled vehicles, residential wood combustion, charbroiling operations, prescribed burning, and wildfires – because they simultaneously emit large fractions of OC. OC is known as a cooling agent that may or may not offset BC.

This overview paper puts BC emissions in context and against the backdrop of California's AB32 efforts. Research activities are highlighted to deal with existing uncertainties related to BC emissions, and their predicted regional climate influence. Knowledge gaps on the chemical and radiative properties of ambient carbonaceous aerosols will also be addressed. Related research findings will be summarized and preliminary estimates for reductions in climate species in California through the year 2020 will be presented. Reduction opportunities for non-Kyoto GHGs are sought when developing air quality regulations and efforts related to carbonaceous aerosols will be emphasized.

* Presenter and corresponding author, (916) 327-2952, aayala@arb.ca.gov

INTER-COMPARISON OF TWO METHODS FOR THE QUANTIFICATION OF « HUMIC LIKE SUBSTANCES » IN ATMOSPHERIC AEROSOL PARTICLES

CHRISTINE BADUEL, D. Voisin, J.-L. Jaffrezo, M. Legrand, Laboratoire de Glaciologie et Géophysique de l'Environnement, CNRS, Université Joseph Fourier-Grenoble, Grenoble, France.

As in any other environmental system containing organic compounds, the atmospheric organic aerosol has been found to be highly chemically complex. A class of organic molecules extracted from atmospheric aerosol has been named **HUmic LIke Substances (HULIS)** because their properties (UV-Vis absorbance, average Molecular Mass, ...) present large similarities with those of terrestrial and aquatic humic and fulvic acids. However, the nature of the different species, their concentrations, sources and modes of formation are still mostly unknown. Almost six different protocols for the separation of HULIS based on physicochemical properties such as their hydrophobic behaviour or their polyacidic nature can be found in literature. Further, depending of the extract protocol, two different quantification methods are used in the literature: UV-Visible or Total Organic Carbon analyser.

It is difficult to evaluate if the different protocols isolate and extract a comparable fraction because inter comparison between these different methods has not been still conducted. With the goal to standardize extracted and quantification methods for this polyacid fraction in the atmosphere, we tested the two main extraction techniques and compare the two quantification method. The first method is that proposed by Decesari et al. (2000). It uses the acidic nature of HULIS compounds. The aerosol extract was concentrated on a DEAE-cellulose eluted in strong NaOH and removing by inorganic salts. The second method is that of Limbeck et al. (2005). They developed a method for carbon-specific determination of HULIS based on a two step isolation procedure, C18 then SAX. Our work will present an inter-comparison of these two methods, focusing on aerosol samples collected at Chamonix (France) during the summer and winter seasons.

MEASUREMENT OF BLACK CARBON AND PARTICLE NUMBER EMISSION FACTORS FROM INDIVIDUAL HEAVY-DUTY TRUCKS

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A significant fraction of black carbon (BC) worldwide is emitted by diesel-fueled motor vehicles. In this study we measured emission factors for BC and particle number (PN) from 226 individual heavy-duty (HD) diesel-fueled trucks in a 1 km-long California highway tunnel in August 2006. Emission factors are based on concurrently measured increases in BC, PN, and CO₂ concentrations (measured at 1 Hz) that correspond to the passage of individual HD trucks. Results demonstrate that the distributions of BC and PN emission factors from individual HD trucks are skewed, meaning that the majority of pollution comes from a small fraction of the in-use vehicle fleet. The highest-emitting 10% of trucks were responsible for ~40% of total BC and PN emissions from all HD trucks. BC emissions were log-normally distributed with a mean emission factor of 1.7 g kg⁻¹ and maximum values on the order of ~10 g kg⁻¹. Corresponding values for PN emission factors were 4.7×10^{15} and 4×10^{16} # kg⁻¹. There was minimal overlap among high-emitters of these two pollutants: only 1 of the 226 HD trucks measured was found to be among the highest 10% for both BC and PN. These findings are consistent with previous studies that showed that emissions of carbon monoxide, nitrogen oxides, and volatile organic compounds from light-duty (LD) gasoline vehicles are skewed. The skewed nature of motor vehicle emissions has important consequences for development of emission inventories and effective emission reduction policies.

THREE CITIES' STUDY OF BIOGENIC EMISSIONS: ANNUAL TREND AND CONTRIBUTION OF WOOD SMOKE AND FUNGAL SPORES TO ORGANIC CARBON IN PM₁₀ AEROSOLS IN AUSTRIA

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INTRODUCTION: Wood smoke has been found to be the most important source of organic carbon in PM₁₀ aerosols in Austrian cities in winter. The concentration of wood smoke is even higher as the concentrations of traffic emissions (diesel-exhaust plus abrasion of tyres and pavement). In summer fungal spores are not only important because of their allergic properties, they form also the most abundant fraction of primary biogenic particles. Quantitative assessments of the amount of wood smoke in Austria (Schmidl et al., 2008) and Europe (Puxbaum et al., 2007) and of concentrations of fungal spores in Austria (Bauer et al., 2008) have been reported recently.

EXPERIMENTAL: The amount of wood smoke as well as the concentrations of fungal spores are derived by using saccharides as tracers, the anhydro-sugar levoglucosan for wood smoke and sugar-alcohol arabitol for fungal spores (Bauer et al., 2008). Samples were collected daily from January to December 2004 with High Volume samplers in three Austrian cities: Vienna, Graz and Salzburg, at a residential and a traffic dominated site in each city. The filters were analyzed for PM₁₀ aerosol mass, total, organic, elemental and carbonate carbon, anhydro-sugars, polyols and ions (major ions and organic acids). The tracers levoglucosan and arabitol were determined in one analytical step using high pH anion exchange and pulsed amperometry (HPAE-PAD). Details of the analytical method are given in Caseiro et al., 2007. Organic carbon was determined as the difference of total carbon minus elemental carbon using thermal methods.

RESULTS: Wood smoke concentrations and fungal spores' concentrations show trends in the opposite direction. Average wood smoke concentrations of 4.3 $\mu\text{g m}^{-3}$ (in terms of OC) and of 0.2 $\mu\text{g m}^{-3}$ were measured in December and in July in the three cities. Concentrations of fungal spores (in terms of OC) ranged between 0.51 $\mu\text{g m}^{-3}$ in July and 0.04 $\mu\text{g m}^{-3}$ in January. In December wood smoke is the strongest source with a contribution of 46% to OC₁₀ while fungal spores account for less than 1%. In July however, fungal spores contribute 15% and wood smoke only 6% to OC₁₀.

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OPTIMIZATION OF SENSITIVE SPME METHOD FOR ANALYSIS OF WATER-SOLUBLE ALDEHYDES

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Methods for characterization of aldehydes in particulate matter (PM) typically involve several steps (derivatization, extraction and solvent evaporation), thus resulting in a time and solvent consuming procedures. The alternative solid phase micro-extraction (SPME), solvent free, pre-concentration technique, may improve the sensitivity as well as facilitate and accelerate the analysis of aldehydes.

In this study, we have optimized a SPME method for a determination of a wide range of water-soluble aldehydes (saturated/unsaturated aliphatic, aromatic aldehydes including hydroxylated species, and dialdehydes) that may be encountered in PM samples. Three SPME techniques (liquid, headspace, and on-fiber derivatization) with *o*-(2,3,4,5,6-pentafluorobenzyl)-hydroxylamine hydrochloride (PFBHA) aldehyde derivatization were evaluated focusing on the optimization of the main extraction parameters (temperature and time).

Despite a thorough optimization, the on-fiber SPME method was not suitable for the determination of a wide range of aldehydes in aqueous solutions due to its inability to recover dialdehydes and hydroxylated aromatic aldehydes (hydroxybenzaldehydes, syringaldehyde). Headspace-SPME of aldehydes (directly derivatized with PFBHA in aqueous solution) recovered all aldehydes, but only at a high extraction temperature (80 °C). Higher temperature apparently improved the partitioning of highly water-soluble compounds (PFBHA derivatized hydroxyl aromatic aldehydes) as well as high-molecular weight (MW) analytes (C₈-C₁₂ derivatized aliphatic aldehydes, dialdehydes derivatized with two PFBHA molecules) out of the aqueous phase.

Liquid SPME (LQ-SPME, i.e., with the fiber submerged into a liquid), involving a direct derivatization of aldehydes in aqueous solution, was able to recover all analytes under any examined extraction conditions. Using the LQ-SPME, partitioning of analytes into the gas-phase was by-passed, as opposed to the headspace and on-fiber SPMEs. However, both thermodynamic and kinetic factors still significantly affected the efficiency of this method, i.e., limits of detection (LODs) and linear concentration ranges. Nonetheless, LQ-SPME at 80 °C with a 30 min long fiber exposure was determined to be the most sensitive method (LODs as low as 0.1 µg/L) for all aldehydes and, thus, was selected for the analysis of aldehydes in aqueous PM extracts (wood smoke, diesel exhaust PM).

Compared to a reference EPA 556 method, which employs liquid-liquid extraction (LLE), optimized LQ-SPME was more sensitive, by 1–2 orders of magnitude. Thus, even trace amounts of aldehydes in PM samples could be quantified while using LQ-SPME. More importantly, LQ-SPME appeared to eliminate some analysis artifacts inherent for LLE. Apparently, *low-MW analytes* were partially lost during the solvent evaporation, an essential re-concentration step in EPA 556 method, thus underestimating their amounts in PM. Concentrations of *dialdehydes*, on the other hand, may be overestimated with EPA 556 method due to the possible conversion of oligomers into their monomer units (i.e., dialdehydes) during LLE. Therefore, LQ-SPME was suggested as a suitable method for the analysis of water-soluble aldehydes in PM samples.

SPECTRAL ABSORPTION BY ATMOSPHERIC CARBONACEOUS PARTICLES

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During several Atmospheric Field Campaigns (PRIDE, SAFARI, ACE-Asia, and INTEx A) the Solar Spectral Flux Radiometer (SSFR) and the 14-channel Ames Airborne Tracking Sunphotometer (AATS-14) have been integrated on the same aircraft to provide complementary measurements for a variety of scientific purposes. The SSFR measures the spectrally resolved net solar irradiance while the AATS 14 measures the aerosol optical depth at discrete wavelengths, water vapor and ozone amounts. We used the combination of these two measurements to determine the spectral absorption properties of atmospheric aerosols. A recent publication, Bergstrom et al (2007)¹, discusses the results from these campaigns. The results show that the aerosol absorption can be approximated with an exponential power law with different aerosol materials having different ranges of exponents.

During the MILAGRO/INTEx-B campaign the two instruments were used on the J31 aircraft for measurements in the region of Mexico City and Veracruz, Mexico. We will present results from this field program for the aerosol spectral single scattering albedo and absorption coefficient. We will compare our results with a number of other measurements of the absorption at ground sites and in situ results. We are focusing on the aerosol absorption in the UV wavelength region as increased absorption has been observed in this spectral region, perhaps caused by organic carbonaceous material. We will also discuss our results in the context of the other previous field experiments.

¹ Bergstrom, R.W., P. Pilewskie, P. B. Russell, J. Redemann, T. C. Bond, P. K. Quinn, and B. Sierau, Spectral absorption properties of atmospheric aerosols, *Atmos. Chem. Phys.*, 7, 5937-5943, (2007).

SIMULATING SECONDARY ORGANIC AEROSOL ACROSS THE UNITED STATES – SENSITIVITY ANALYSES USING THE CMAQ MODEL

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The U.S. EPA's Community Multi-scale Air Quality (CMAQ) modeling system has been updated to treat secondary organic aerosol (SOA) formation from several recently-identified precursors (benzene, isoprene, and sesquiterpenes) and pathways (in-cloud oxidation, polymerization, and an acid-catalyzed process), along with the dependence of aromatic SOA yields on nitrogen oxide concentrations and new empirical measurements of the enthalpies of vaporization. Due to the absence of direct SOA measurements, progress in SOA modeling has been judged mainly via comparisons with bulk measurements of total carbon, organic carbon, or water-soluble organic carbon. A newly developed organic tracer-based method provides the first quantitative estimates of ambient concentrations of SOA from aromatics, isoprene, monoterpenes, and sesquiterpenes (Kleindienst et al., 2007), thereby permitting the most source-specific assessment of SOA models to date.

Preliminary results from a 3-week summertime CMAQ simulation have been evaluated against tracer-based estimates in Research Triangle Park, North Carolina. The tracer-based estimates averaged over this period indicate a biogenic SOA concentration of 2.7 $\mu\text{gC}/\text{m}^3$, with roughly equal contributions from isoprene, monoterpenes, and sesquiterpenes. Model results also show a roughly equal contribution from these three precursors, but their total SOA production is relatively low (0.6 $\mu\text{gC}/\text{m}^3$). Likewise, modeled concentrations of aromatic SOA fall short of the tracer-based values (0.11 vs. 0.63 $\mu\text{gC}/\text{m}^3$). These comparisons indicate that the CMAQ modeling system underestimates SOA contributions from all four of the precursor classes considered here. Model results exhibit similar underpredictions when compared with tracer-based SOA estimates made at five Midwestern sites during summer 2004.

In this study, we will repeat the CMAQ simulation with a variety of parameters to explore several hypotheses for reconciling the differences between modeled and tracer-based SOA concentrations. First, we will examine the possibility that the model bias is arising from an incorrect translation of chamber-based yields into air quality models (Jiang, 2003). Second, we will examine whether laboratory yield data other than those upon which our model formulation is based would increase the modeled SOA concentrations. Third, we will test the effects of alternative biogenic emission factors (Sakulyanontvittaya et al., 2008) on CMAQ model performance. Fourth, we will study the volatility distribution of our model results to explore the possibility that organic compounds with "intermediate" volatility (Robinson et al., 2007) may be the missing SOA source.

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REVISITING THERMAL-OPTICAL ANALYSES OF CARBONACEOUS AEROSOL WITH A PHYSICAL MODEL

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I attended my first ICCPA eight years ago, a relative newcomer to this field. One of the last sessions I saw at that conference focused on artifacts in organic and elemental carbon analysis. By the end of the session, I thought my head was going to explode! I couldn't imagine how anyone could bear the constant onslaught of artifact mechanisms. That experience led to an item on my to-do list, then to a series of items, then to a proposal and finally to a project. The work presented here is the result.

The composition of a sample, organic or elemental carbon, may be thought of as a solution to physical equations that represent the response of the analysis system. The conundrum of thermal-optical analysis lies in the fact that more than one sample composition is physically consistent with the system's response. The iterative model presented here ((REAnalyzing Carbon Traces Optically, or REACTO) identifies the range of sample composition that is consistent with the analyzer's response. The guiding parameters for interpreting the model were developed by examining real-time analyses of hundreds of samples from diesel engines, wood burning, and model compounds.

REACTO may be published by the time we meet in Berkeley, so my presentation won't be very novel. This presentation has a different goal: to enlist you, the audience, in contributing sample analyses that can provide further constraints. My few hundred source samples represent a very small subset of the universe of carbonaceous aerosol samples. REACTO is hungry for your raw data files, especially those produced by the Sunset OC/EC analyzer, and particularly those with both transmittance and reflectance monitoring. We are particularly interested in looking at samples of secondary organic aerosol, and those known to be dominated by particular sources.

COMPARISON OF NEAR-ROADWAY CARBON MEASUREMENTS IN WINTER IN LAS VEGAS

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During January 2008, measurements were conducted at Fyfe Elementary School in Las Vegas, Nevada, to understand the nature of pollutants near a roadway. The sampling inlets were approximately 22 m from the soundwall of U.S. 95. Measurements included high time-resolution $PM_{2.5}$ with an Aerodyne high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS), hourly carbon with a Sunset OCEC analyzer, 5-minute absorption at multiple wavelengths (black carbon [BC] and UV) with an AethalometerTM, and 5-minute particulate polycyclic aromatic hydrocarbons (pPAHs). These data allow for a comparison among multiple measures of carbon. Measurements of AMS organic matter (OM), Sunset OC and EC, Aethalometer BC and pPAH were examined for diurnal and weekday-weekend patterns and differences. Comparisons among measurements by wind direction and speed were also examined. Ambient aerosol was typically dominated by the nearby freeway emissions, though periods of wood smoke influence were seen on some Friday and Saturday evenings. A strong relationship was observed between primary pollutants and markers throughout the day and with wind direction and speed. For example, BC was well correlated with NO and CO. These species also tracked well with pPAH and total OC, as well as with an indicator of primary OC from the AMS (m/z of 57), suggesting much of the OC is primary. Within an hour's time period, the best resolution of the Sunset OCEC data, the AMS, PAH and BC data all showed significant variations in concentrations during most hours of the day. Depending on time of day, day of week, and synoptic weather patterns, different regimes were seen influencing the carbon concentrations: (1) mostly primary aerosol associated with the freeway (low OC/EC ratio, high degree of primary influence, higher PAH and BC concentrations); (2) secondary regional or urban influence (higher ammonium nitrate concentrations, high OC/EC ratio, higher signal of a secondary OC AMS marker); and (3) weekend evenings/overnight influenced by wood smoke and/or freeway (wood smoke markers observed in the AMS data, mix of OC/EC ratios, high concentrations of PAH, BC).

BIAS IN FILTER BASED AEROSOL ABSORPTION MEASUREMENTS DUE TO ORGANIC AEROSOL LOADING: EVIDENCE FROM LABORATORY AND FIELD MEASUREMENTS

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The absorption and scattering of light by aerosol particles in the atmosphere play key roles in determining the radiative balance of the Earth. Absorbing aerosol, unlike purely scattering aerosols, can heat or cool the atmosphere depending on the fraction of absorption relative to scattering. Aerosol absorption usually comprises a small fraction of the total light attenuated by the aerosol, and thus can be difficult to measure accurately. To date, the most common in situ measurement of aerosol particle absorption has been obtained using filter based methods, such as the particle soot absorption photometer (PSAP), the aethelometer and the multi-angle absorption photometer (MAAP). These filter-based measurements are known to require various corrections, which are unique to each technique and attempt to account for changes in the filter properties upon loading with aerosols, for scattering losses and for absorption enhancements. More recently, photo-acoustic spectroscopy (PAS) and photo-thermal interferometry have been used to measure light absorption by particles. PAS can be considered an appropriate standard with which to assess the performance of the filter-based techniques because the aerosol is sampled in suspension, without the need for collection on a filter.

Here we present results from both field observations and laboratory experiments that demonstrate that the relative agreement between the light absorption derived from a PSAP (b_{PSAP}) and from a PAS (b_{PAS}) depends explicitly on the concurrent abundance of organic aerosol. The ratio $R_{abs} = b_{PSAP}/b_{PAS}$ was found to increase strongly as the amount of organic aerosol increased. The field observations were made on board the R/V Ronald H. Brown during the TexAQS/GoMACCS 2006 field campaign over a period of 37 days. The laboratory studies were carried out using external mixtures of strongly absorbing aerosol (either nigrosin dye particles or flame-generated soot) with essentially non-absorbing secondary organic aerosol (generated from the reaction of α -pinene with O_3). In the field study, the highest R_{abs} values observed were > 3 and corresponded to OA concentrations of $\sim 15 \mu\text{g}/\text{m}^3$, or OA/LAC mass ratios of ~ 50 , where LAC is light absorbing carbon. The laboratory experiments results were quantitatively consistent with the field observations and support the idea that the observed discrepancy results from a bias in the PSAP measurement and not in the PAS measurement. Additionally, the lab experiments explicitly demonstrated that the standard filter transmission corrections that are used for the PSAP are not applicable to loading of the filter with organic aerosol. The results of these studies indicate that it may be necessary to explicitly consider the aerosol composition in determining an appropriate correction scheme to use when filter based methods are used to measure light absorption by aerosols. In light of these results, it may be necessary to revisit long-term time series measurements of light absorption made using PSAP's as they may be biased by concurrent changes in the OA abundance

USE OF PROTON BACKSCATTERING TO DETERMINE THE CARBON CONTENT IN SAMPLES DEPOSITED ON TEFLON FILTERS

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Particulate carbon is routinely measured in the IMPROVE (Interagency Monitoring of Protected Visual Environments) program by analysis of particles collected on quartz filters. The analysis is performed at Desert Research Institute using the Thermal Optical Reflectance method. Measurements of Si, Al, Ca, Ti, and Fe by X-ray fluorescence at Crocker Nuclear Laboratory are used by IMPROVE to calculate a SOIL parameter by weighting these elements to account for the oxygen that is not measured. It is desirable to have alternative methods to measure both carbon and oxygen for data validation purposes.

We have tested a method to measure carbon and oxygen concentrations from air samples deposited on Teflon membrane filters using the backscattered proton spectrum. The measurements were performed with a 4.5 MeV proton beam from the cyclotron of the Crocker Nuclear Laboratory during routine IMPROVE measurements of hydrogen by Proton Elastic Scattering Analysis. A surface barrier detector at 155° below the plane of the beam was employed in a Cornell geometry setup to measure the proton spectrum. We will discuss a consistent method to estimate the carbon from the Teflon filter substrate that must be subtracted from the measured carbon (filter plus deposit). This method is independent of the number and arrangement of the fibers and the unknown stretching of the substrate. We have measured carbon at multiple IMPROVE sites using this new method and will compare these results with the results using Thermal Optical Reflectance. We will also compare the gravimetric mass to the sum of all elements, including the oxygen and carbon determined by proton backscattering.

TOWARD A STANDARDIZED THERMAL-OPTICAL PROTOCOL FOR MEASURING ATMOSPHERIC ORGANIC AND ELEMENTAL CARBON: THE EUSAAR PROTOCOL

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Measurement of atmospheric elemental carbon (EC) has long been problematic largely due to the fact that its chemical, physical, and morphological nature is complex and variable. Methods based on thermal-optical analysis are widely used for elemental carbon determination in aerosol samples. Nevertheless, different thermal evolution protocols result in wide elemental carbon to-total-carbon variation.

In Europe, there is currently no standard procedure for analysing carbonaceous aerosol fraction, which implies that data obtained by different laboratories at various sites are most likely not comparable and affected by unknown errors. In the framework of the European project EUSAAR (European Supersites for Atmospheric Aerosol Research), an accurate work has been carried out to investigate the causes of differences in the EC measured using different thermal evolution protocols and attempts have been devoted to assess and mitigate major positive and negative biases affecting thermal-optical analysis.

Our approach to improve the accuracy of the thermal-optical discrimination between organic carbon and EC was essentially based on three goals. First, as charring correction relies on assumptions proved to be generally not true –e.g. equal specific cross section values of pyrolytic carbon and elemental carbon–, we sought to reduce pyrolysis to minimum levels in favor of a maximum volatilisation of organic carbon. Second, we sought to minimize the potential (negative) bias in EC determination caused by the release of light absorbing species at high temperature in the He-mode, including native EC or a combination of EC and pyrolytic carbon with potentially different specific cross section values. Third, we sought to minimize the potential positive bias in EC determination resulting from the slipping of residual organic carbon into the He/O₂-mode and its potential evolution after the split point.

The work here presented led to the definition of an improved thermal evolution protocol, the EUSAAR protocol: step 1 in He, 200 °C for 120 s; step 2 in He 300°C for 150s; step 3 in He 450°C for 180s; step 4 in He 650°C for 180s. For steps 1-4 in He/O₂, the conditions are 500°C for 120s, 550°C for 120s, 700°C for 70s, and 850°C for 80s, respectively.

FRACMAP: A GRAPHICAL USER-INTERACTIVE PACKAGE FOR PERFORMING SIMULATION AND ORIENTATION-SPECIFIC MORPHOLOGICAL ANALYSIS OF FRACTAL-LIKE AEROSOL AGGLOMERATES

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Carbonaceous aerosols produced by high temperature combustion processes generally take the shape of fractal-like chain aggregates. Computer simulation techniques have proven to be quite useful for studying the structure of such agglomerates produced by aggregation of smaller particles (monomers) and for establishing empirical relationships between their three dimensional (3-d) and two dimensional (2-d) projected properties. We describe a software package, *FracMAP*, which has been written to simulate the aggregation of monomers into monodisperse agglomerates in 3-d space using the Monte Carlo method. Making use of a highly efficient algorithm, the code generates all possible projections (similar to images from electron-microscopy) of 3-d agglomerate onto a 2-d plane. Projections can also be constrained by requiring a stable orientation of the 3-d agglomerate such as encountered if it is collected on a filter substrate.

This code is coupled to a graphical user interface, thereby enabling the user to input all the necessary parameters for the generation of 3-d agglomerates. These 3-d agglomerate and their 2-d projections can also be graphically displayed for visual inspection. The program has various subroutines for performing structural and fractal analysis of the agglomerates in both 2-d and 3-d. These subroutines are presented as options on the user-interface screen. Based on user input, the program calls for the specific subroutines, executes them, and returns the structural analysis results to the user. *FracMAP* is written in C++, and the program has been tested to run successfully under UNIX and WINDOWS operating systems.

MORPHOLOGY AND EFFECTIVE REFRACTIVE INDICES OF AEROSOLS EMITTED FROM HIGH-MOISTURE-CONTENT BIOMASS COMBUSTION

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Emissions from the combustion of wildland fuels are a major source of carbonaceous aerosols in the atmosphere. Satellites are commonly used for remotely quantifying aerosol concentrations in the atmosphere and for studying aerosols radiative effects on global and regional scales. The quality of satellite aerosol retrievals depends critically upon the modeling of the aerosol optical properties, which strongly depend on the particle Effective Index of Refraction (EIR). EIR is generally used to account for the composite internal and external mixing state of particles. However, little is known about the EIR of aerosols emitted from the combustion of wildland fuels. As part of a study conducted in May-June 2006 at the USFS (U.S. Forest Service) Fire Sciences Laboratory investigating properties of aerosols emitted by fires, we studied the optical properties, size distribution, and morphology of particles emitted from the combustion of many common wildland fuels. Ensemble particle absorption and integrated scattering properties were determined using photoacoustic-spectrometer/nephelometer technique at three different wavelengths, 405, 532, and 870 nm. The particle size distribution was continuously monitored using an ELPI (Electrical Low Pressure Impactor), while the morphology was studied with scanning electron microscopy. It was found that combustion of three high moisture containing wildland fuels (Fresh Montana Grass, Ponderosa Pine Duff, and Alaskan Duff) produced near spherical particles. The near sphericity of the particles facilitates the analysis of the absorption and scattering data and permits using Mie theory to derive real and imaginary parts of EIRs. The procedure and results of the analysis for each of the fuels will be presented.

LIGHT ABSORPTION BY ORGANIC CARBON FROM WOOD COMBUSTION

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Carbonaceous aerosols are prevalent in urban areas and affect the radiative balance of the Earth by absorbing and scattering light. Carbonaceous aerosol is composed of black carbon (BC) and various types of organic carbon (OC). It is well known that BC is the most absorbing aerosol in the atmosphere. The role of OC in light absorption has been less investigated, but some organic compounds also have significant absorption, which is greater at near-ultraviolet and blue wavelengths. Since visible absorption is far more important for the energy balance than ultraviolet absorption, to the extent that OC absorbs visible light, it may be a non-negligible contributor to direct aerosol radiative forcing. In this work, we examine primary OC emitted from solid fuels, which provide about two-thirds of global primary organic aerosol emissions. Our work focuses on understanding the chemical composition and optical properties of these particles in order to better characterize them in models, especially how these properties depend on the generation variables. We provide absorption spectra of OC in bulk liquid extracts, which can be related to optical properties of OC particles. Further fractionation of OC extracts based on polarity of organic compounds can help us understand the hygroscopic properties of OC.

Samples were generated in a laboratory combustion chamber at different temperatures using various sizes of softwood and hardwood, and collected on baked quartz filters. The filters were then extracted with deionized water and different organic solvents, including methanol, hexane and acetone. Light absorption of different sample solutions was tested at the wavelength from 190nm to 800nm. Absorption spectra of the extracts were measured with a Shimadzu UV-2401 UV-Vis recording spectrophotometer. Total carbon was measured with a Sunset OC/EC analyzer. More than 95% mass of total carbon could be extracted by methanol or acetone, compared with 72% for water and 59% for hexane. Our results showed that light absorption in visible spectrum was partially caused by water soluble organic carbon and another larger portion was caused by organic carbon that is water insoluble, but somehow polar. The greatest absorption per mass of carbon at 400nm was found in methanol and acetone extracts, which is 2.5 times of that in water extracts, and 1.8 times of that in hexane extracts. Absorption depends on combustion variables, including wood type, wood size and pyrolysis temperature. Higher temperatures and longer residence time of volatile matter in the wood create high absorption organic materials.

ANALYSIS OF CARBON IN AEROSOL SAMPLES WITH ACCELERATED PROTON BEAMS

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Ion Beam Analysis (IBA) techniques have proven to be a reliable tool to study the composition of atmospheric aerosol in a fast, non-destructive way. In particular, Particle Elastic Scattering Analysis (PESA) technique, based on the detection of the beam particles elastically scattered by the target nuclei, allows one to obtain quantitative information about the elemental composition of the sample as regards low Z atoms like Carbon, as well as Hydrogen, Nitrogen and Oxygen. Coupled to Particle Induced X-ray Emission (PIXE) measurements to determine the concentration of elements with $Z > 10$, it allows a complete reconstruction of the aerosol mass.

This methodological technique was successfully implemented at the old 3 MV single-ended Van de Graaff accelerator in Florence, Italy, using proton beams of 3 MeV energy. In this work we will show the improvements in PESA analysis of Carbon in particulate matter samples collected on Teflon filters accomplished with the new 3 MV Tandem accelerator of LABEC laboratory of INFN in Florence. In particular, we will discuss the possibility of PESA measurements with higher proton beam energies (up to 6 MeV) and we will introduce a new self-consistent data analysis procedure based on the detection of the inelastically scattered protons.

We will also present the results of the first inter-comparison between PESA and thermo-optical-transmittance analyses for measuring the Total Carbon in particulate matter samples collected in parallel on both Teflon and Quartz fibre filters, during a field campaign organised in October 2006 in two sites in Tuscany, Italy.

CARBONACEOUS COMPONENTS IN PM10 IN TUSCANY (ITALY): RESULTS OF A YEAR LONG CAMPAIGN

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In the framework of the PATOS research project (Atmospheric Particulate in Tuscany), PM10 daily samples were collected in six different sites in the region of Tuscany (Italy) during one year, from September 2005 to September 2006. Three different typologies of sites were selected: urban-traffic (Arezzo, Prato, Lucca), urban-background (Florence, Grosseto) and suburban-background (Livorno). All the samples were collected with low-volume samplers (FAI Hydra Dual Sampler) in parallel on both Teflon and Quartz fibre filters, the latter for the analysis of the carbonaceous components of atmospheric aerosol.

Total Carbon (TC) was obtained by a CHN elemental analyzer (Thermo 1112); Organic Carbon (OC) and Elemental Carbon (EC) were determined using the same instrument after acid and thermal treatment of the sampled filters, following the methodology proposed by Zappoli et al. [Atm. Env. 33 (1999) 2733]. An inter-comparison between CHN and thermo-optical-transmittance analyses for TC, OC and EC was performed on a selected subset of samples. The spatial and seasonal patterns for TC, OC and EC were investigated to obtain information about the sources of particulate matter and to allow the Regional Government to issue regulations aimed at emission reduction.

In all the investigated sites the samples showed a high percentage of Particulate Organic Matter (POM), ranging from 35% to 50% of the PM10 total mass. Moreover, in all the urban sites the POM concentrations resulted higher in wintertime, when the emissions by domestic heating added to the vehicular emissions (and more stable meteorological conditions occurred). Minimum seasonal variation was observed only in the suburban site, Livorno.

Secondary Organic Carbon was estimated as well, using the approach proposed by Turpin and Huntzicker [Atm. Env. 23 (1995) 3527]. In general, this component resulted lower during the cold season.

Assessment of Carbon Sampling Artifacts in the IMPROVE, STN/CSN, and SEARCH Networks

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Abstract

The adsorption of volatile and semi-volatile organic compounds (VOCs and SVOCs) on quartz-fiber filters during collection of PM_{2.5} and PM₁₀ samples for thermal/optical carbon analysis results in artifacts that complicate estimates of both organic carbon (OC) and elemental carbon (EC). The magnitude of this sampling artifact depends on sampling protocol, which varies among ambient networks. Field blanks (bQF) and quartz-fiber backup filters behind quartz-fiber front filters (QBQ) were used to compare and evaluate the sampling artifact estimation by the carbon analysis protocols used in the IMPROVE, STN/CSN, and SEARCH networks. IMPROVE field blank OC were in the range of 2.0 – 2.5 $\mu\text{g}/\text{cm}^2$, while both STN/CSN and SEARCH were closer to 1 $\mu\text{g}/\text{cm}^2$. This difference is consistent with shorter passive exposure periods utilized by the latter networks, which is insufficient to allow complete diffusion of organic vapors through the filters. The magnitude of QBQ OC is a function of sampling face velocity, sampling duration, temperature and relative humidity, in addition to ambient VOC/SVOC concentration. OC loadings on QBQ were found to be similar to those on concurrent bQF for the rural IMPROVE sites, but were substantially higher for urban sites. Comparisons between urban and rural sites among the SEARCH network show an average OC on QBQ that is 22% higher at the urban sites. Aerosol aging may also be a factor which influences the organic sampling artifact, i.e. the increase of aerosol aging may reduce SVOC content and hence the positive and/or negative organic sampling artifacts.

CHARACTERIZATION OF ORGANOSULFATES AND NITROOXY ORGANOSULFATES FROM THE PHOTOOXIDATION OF ISOPRENE AND UNSATURATED FATTY ACIDS IN AMBIENT FINE AEROSOL

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Molecular characterization of organic aerosol constituents in the atmosphere is important because it allows one to gain insights into aerosol sources and the underlying mechanisms of secondary organic aerosol (SOA) formation. In the present study, a range of novel polar organosulfates and corresponding nitrate derivatives were structurally characterized in SOA from the photooxidation of isoprene, a biogenic volatile organic compound that is emitted from the vegetation in large quantities (estimated at about 500 Tg per year on a global scale), and subsequently detected in ambient fine aerosol. In addition, a number of unknown compounds with hydrophilic properties comparable to those of the isoprene-related organosulfates were structurally characterized and tentatively identified as SOA from the photooxidation of unsaturated fatty acids.

SOA from isoprene was generated in environmental chambers under atmospherically relevant conditions, i.e., in the presence of NO_x (low to high concentrations) and sulfuric acid seed aerosol. The techniques employed for structural characterization of organosulfates and nitrooxy organosulfates were based on high-performance liquid chromatography/negative ion electrospray ionization mass spectrometry [LC/(-)ESI-MS]. They included LC/(-)ESI-high resolution MS using an LCT Premier XT time-of-flight instrument (Waters) for obtaining accurate mass data and LC/(-)ESI-linear ion trap MS using an LXQ instrument (Thermo Fisher) for obtaining MS²/MS³ product ion spectra. LC separation of the very polar isoprene SOA organosulfate derivatives was achieved with a stationary phase containing di- or trifunctionally bonded C₁₈ residues.

Accurate mass data obtained on deprotonated molecules [M - H]⁻ with an accuracy of about 0.2 mDa were used to infer or support molecular formulae, while MS²/MS³ data were used to propose or verify chemical structures. Organosulfates were identified on the basis of a *m/z* 97 ion [HSO₄⁻] or the loss of 80 u (SO₃) in their [M - H]⁻ MS² spectra, while organosulfates containing an additional nitrate group were characterized by a loss of 63 u (HNO₃) in their [M - H]⁻ MS² spectra and fragmentation to a *m/z* 97 [HSO₄⁻] product ion in a subsequent MS³ experiment. In selected cases, MS³ experiments were also carried out on the product ion resulting from the neutral loss of SO₃. Following this approach, organosulfates and nitrooxy organosulfates from novel isoprene SOA products could be characterized which subsequently were also detected in ambient fine aerosol from the southeastern USA, i.e., (i) a C₅-alkane triol (2-methyl-1,2,3-trihydroxybutane and a positional isomer) mixed sulfate/nitrate derivative (MW 245), (ii) sulfate derivatives of hemiacetal dimers (isomeric mixture) formed between 2-methyltetrols and a C₅-dihydroxycarbonyl (2,3-dihydroxy-2-methylbutane-1-one) (MW 334), and (iii) 2-methyltetrol mixed sulfate/dinitrate derivatives (MW 306).

In addition to organosulfates from isoprene SOA, very polar organosulfates that likely arise from the photooxidation of plant leaf volatiles such as for example Z-3-hexenal, which result from enzymatically released unsaturated fatty acids when plants are wounded, could also be tentatively identified.

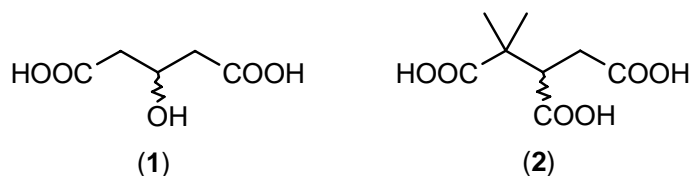
CHARACTERIZATION OF NOVEL TRACERS FOR α -/ β -PINENE SECONDARY ORGANIC AEROSOL

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Considerable efforts have been devoted in the last two decades to gain insights into secondary organic aerosol (SOA) formation from the photooxidation of volatile organic compounds (VOCs), in particular, the monoterpene, α -pinene. It has been firmly established that *cis*-pinic and *cis*-pinonic acid are major products formed by reaction of α -/ β -pinene with ozone. However, several ambient aerosol studies have shown that the atmospheric concentrations of these SOA tracers are rather low during summer episodes, while evidence was obtained that highly oxygenated products are formed that could also be generated by irradiating α -/ β -pinene in the presence of NO_x through reactions that involve ozone and OH radicals. In the present communication, we address the chemical identification of two major α -/ β -pinene SOA tracers with MWs 148 and 204. The structure elucidations of both compounds have posed an analytical challenge because the pinene skeleton is not retained.

Archived $\text{PM}_{2.5}$ samples collected from K-pusztá, Hungary, during a 2003 summer campaign and from three different sites in the USA during the summer 2004 Southeastern Aerosol Research and Characterization Study, were used. Laboratory samples were obtained by irradiating VOC mixtures containing α -pinene in the presence of air and NO_x . The samples were extracted with methanol under ultrasonic agitation. Several complementary analytical techniques were employed for structural characterization, including gas chromatography/mass spectrometry with prior derivatization, liquid chromatography/negative ion electrospray ionization mass spectrometry [LC/(-)ESI-MS] and ultra-performance LC/(-)ESI-high resolution MS. The structures of the α -pinene SOA tracers with MWs 148 and 204 were proposed on the basis of detailed interpretation of MS data, and were subsequently confirmed by synthesis of authentic reference compounds.

The α -pinene SOA tracer with MW 148 was elucidated as 3-hydroxyglutaric acid (**1**), while that with MW 204 was firmly established as 3-methyl-1,2,3-butanetricarboxylic acid (**2**).



The formation of both compounds can be explained through further reaction of *cis*-pinonic acid involving participation of the OH radical. Their detection in $\text{PM}_{2.5}$ aerosol illustrates that complex multi-generation chemistry characterizes the photooxidation of α - and β -pinene in the ambient atmosphere. Our study also provides an explanation for the relatively low atmospheric PM concentrations of *cis*-pinic and *cis*-pinonic acid measured in summer that were reported in previous ambient aerosol studies conducted at different sites, both in Europe and the United States.

EVIDENCE FOR MARINE PRODUCTION OF ORGANOSULFATES FROM C₉ – C₁₁ HYDROXY ACIDS

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Organosulfates are a novel group of secondary organic aerosol (SOA) constituents that have only been recently reported in SOA from the photooxidation of isoprene and α -pinene as well as in ambient fine aerosol (Surratt et al., 2007). They are formed in the presence of sulfuric acid seed aerosol and have been suggested as ambient tracer compounds for SOA formation under acidic conditions. In the present study, we demonstrate that organosulfates are also formed in a marine environment during summer conditions that are characterized by algal blooms.

Aerosol samples were collected at Amsterdam Island (37.52 °S, 77.32 °E), a pristine marine site in the Southern Ocean, located about half-way between the southern edges of South Africa and Australia. A high-volume dichotomous sampler was deployed which provides two size fractions, fine and coarse, with a separation between both at 2.5 μ m aerodynamic diameter. The collections were performed from 3 December 2006 till 4 March 2007, the collection time per sample was 5 days, and a total of 18 samples were obtained. All samples were analyzed for organic carbon and elemental carbon with a thermal-optical transmission technique, for water-soluble organic carbon (WSOC) with a Total Organic Carbon analyzer, for water-soluble cationic and anionic species, including methanesulfonic acid (MSA) and dicarboxylic acids, by ion chromatography, and for MSA and additional organic compounds by liquid chromatography/mass spectrometry with electrospray ionization detection in the negative ion mode. Using the latter technique organosulfates of isomeric C₉ – C₁₁ hydroxy acids were detected and structurally characterized.

The molecular weights of the organosulfates of the C₉ – C₁₁ hydroxy acids (254, 268 and 282) were inferred from the m/z values of their deprotonated molecules $[M - H]^-$; the $[M - H]^-$ isotopic pattern indicated the presence of sulfur and multiple oxygen atoms. Ion trap fragmentation of the deprotonated molecules resulted in the formation of the bisulfate ion $[\text{HSO}_4]^-$ (m/z 97), indicating a sulfate group, and the neutral loss of SO₃ (80 u), consistent with the presence of a carboxyl group.

The organosulfates could be detected in all fine samples, but were only quantified in the first 5 samples where their signals were the largest. Using camphorsulfonic acid as a surrogate standard their atmospheric concentrations were estimated at between 0.4 and 2.2 ng C m⁻³ (corresponding to between 1 and 5% of the WSOC). The MSA concentrations in the fine size fraction ranged from 3.4 to 10 ng C m⁻³ (on average, 20 \pm 8 % of the WSOC). Interestingly, the organosulfates showed a different time course than MSA, suggesting a different biogenic source process. The hydroxy acids likely result from the photooxidation of hydroxylated unsaturated fatty acids present in algal biomass. It is clear that MSA and the organosulfates only explain a fraction of the WSOC. However, they both could contribute to the cloud condensation nuclei effects that have been observed above algal bloom regions and have been attributed to SOA from biogenic emissions (Meskhidze and Nenes, 2006).

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Combustion Aerosol as a source of CCN on global scales: Amazon Biomass Burning and Other Continental Sources

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During August of 2007 the Pacific Atmospheric Sulfur Experiment (PASE) investigated the sulfur cycle using 13 NCAR C-130 aircraft missions based out of Christmas Is. (2N, 157W). Part of this study examined the origin and evolution of aerosol in the cloudy equatorial marine boundary layer, MBL, and their relation to effective cloud condensation nuclei, CCN. These data confirm that many of these particles originate through nucleation in the free troposphere, FT, and are entrained into the MBL where they contribute to the MBL particle number. Many particles in the equatorial FT appear to be volatile sulfates generated in cloud outflow that entrain into the MBL with number mean diameters near 50nm and then grow by heterogeneous nucleation to CCN sizes.

However, another significant number fraction with refractory (non-volatile) aerosol component (stable at 300°C) were found to co-vary with ozone and CO in this clean region and were related to the long range transport of particles in the FT with the apparent source being biomass burning in the Amazon, 10,000km distant. They contributed significantly to total number but with a number mean diameter of 60-80nm were associated with little mass, suggesting they were the residual aerosol from cloud scavenged air. Near combustions sources such refractory aerosol are linearly correlated with black carbon, BC, concentrations. Accumulation of a volatile sulfate component during aging and transport made them favorable CCN at low supersaturation near $S=0.2\%$, common for tropical trade-wind non-precipitating clouds. These FT particles were measured as a monomodal number distribution that subsided and then evolve into bimodal number distributions in response to cloud processing in the buffer (cloud) layer and subsequently into the MBL. Particles in the MBL increased their mass through heterogeneous gas to particle conversion primarily linked to the sulfur cycle. Non-precipitating MBL clouds act as a chemical factory for gas-to-particle conversion and result in the development in a "Hoppel" minima near $0.08\ \mu\text{m}$. This preferentially adds mass to these larger sizes more readily activated as CCN. Up to 40% of Pacific Equatorial MBL CCN appeared linked to this distant combustion source.

A reevaluation of over 1,000 airborne vertical profiles of similar refractory aerosol and their links to CO were done for a dozen earlier field studies over the past 15 years. Enhanced refractory number associated with enhanced CO was a common feature, indicative of these being refractory BC and some refractory OC aerosol. The data suggests such combustion derived nuclei act can escape removal from initial convection and survive in the FY as seed particles for deposition of soluble components making them effective CCN and suggesting their influence over global scales. The contribution to remote MBL CCN from sources such as nucleation in cloud outflow and wind driven sea-salt must also include continental combustion. This can be expected to vary with the presence of FT pollution, entrainment rates, surface wind speeds and MBL processes. Reliable estimates of CCN in the MBL must reflect the dynamic interplay of these processes.

RELATIONSHIP BETWEEN OC, EC AND BC CONTENT OF PM₁₀ AEROSOL FROM A NEW ZEALAND URBAN AIRSHED SUBJECT TO AIR POLLUTION EVENTS DURING WINTER

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Carbonaceous aerosols contribute the bulk of the mass of air particulate matter (APM) during air pollution episodes at urban locations in New Zealand, primarily during winter. Receptor modelling studies at several locations around New Zealand have generally used black carbon (BC) as a proxy measurement of elemental carbon (EC) collected on filters to represent combustion source contributions to APM. Organic carbonaceous compounds (OC) generated by combustion sources can also contribute significantly to total PM₁₀ mass depending on the nature of source type. This paper presents the results of OC, EC and BC determination in PM₁₀, PM_{10-2.5} and PM_{2.5} at an urban valley location subject air pollution events during winter inversion conditions. OC/EC concentrations were determined using the IMPROVE protocol for thermal/optical reflectance (TOR) and BC was determined by a light reflectance method. The results show good correlation between the carbonaceous species. The relative ratios of OC to EC were diagnostic of wood burning for domestic home heating as the primary source of combustion emissions during pollution events. In addition, organic compound speciation of PM₁₀ samples by GC/MS suggests that even at PM₁₀ concentrations below the National Environmental Standard (NES) of 50 µg m⁻³, potentially toxic compounds such as polyaromatic hydrocarbons (PAHs) may exceed their respective human health guidelines. The results have implications for air quality management and the protection of health for exposed populations.

Key words: PM₁₀, PM_{2.5}, OC, EC, BC, organic compound speciation

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SECONDARY ORGANIC AEROSOLS FROM ANTHROPOGENIC PRECURSORS: BRIDGING FIELD AND SMOG CHAMBER OBSERVATIONS.

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Aromatic hydrocarbons are an important class of VOCs emitted to the troposphere from anthropogenic activities. Photo oxidation of aromatic hydrocarbons is believed to make a significant contribution to the burden of secondary organic aerosol but the formation mechanisms are yet poorly understood. In the frame of the EU-funded project PolySOA a suite of state-of-the-art analytical methods were employed to investigate the nature of SOA produced in smog chamber by oxidation of 1,3,5-trimethylbenzene (TMB) as model for anthropogenic reactive gaseous pollutants. Moreover, selected ambient SOA were collected on filter substrates and their organic composition investigated with the aim of comparison with those produced in chamber. Total Carbon (TC) and Water-Soluble Organic Carbon (WSOC) have been measured. Anion exchange liquid chromatography was employed for quantitatively resolving WSOC into the following main chemical classes: neutrals (N), mono- and di-acids (MDA) and polyacids (PA). Results indicate that TMB SOA are mainly formed by water-soluble organic compounds, mostly neutral or carrying one carboxylic group per molecule, although dicarboxylic acids also contribute. Polyacids, also called humic-like substances (HULIS), were found only in trace amounts in laboratory SOA despite of their abundance in ambient SOA.

Proton Nuclear Magnetic Resonance (^1H -NMR) spectroscopy was exploited for functional group characterization of TMB SOA, showing prevalently aliphatic compounds with characteristic methyl substituents and carrying alcohols and ether groups. Conversely, water-soluble organic compounds in ambient polluted samples show significant concentrations of aromatics moieties and of aliphatic methylenic chains, together with a higher content of carbonyls and carboxyls respect to laboratory-generated SOA..

Significant differences in overall spectral fingerprints and in chemical classes composition between TMB and ambient SOA strongly suggest that a single hydrocarbon precursor could be not sufficient to reproduce the complex chemistry of real environments.

SECONDARY ORGANIC AEROSOLS FROM BIOGENIC PRECURSORS: BRIDGING FIELD AND SMOG CHAMBER OBSERVATIONS.

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Photochemical processing of biogenic VOCs is the most important global source of secondary organic aerosol (SOA) in the atmosphere. Here we present new results of chemical characterization of SOA produced in smog chambers from the terpenes oxidation and we compare them with the results obtained on ambient SOA samples collected in pristine forested environments. In the framework of the projects PolySOA and EUCAARI, SOA were produced in the PSI and SAPHIR smog chambers by photooxidation of α -pinene, or mixtures of monoterpenes, or monoterpenes with sesquiterpenes. SOA composition was investigated in different ranges of precursor concentration.

A suite of spectroscopic and chromatographic methods were employed to investigate the chemical composition of SOA collected on various filter substrates. Total Carbon (TC) and Water-Soluble Organic Carbon (WSOC) have been measured. Anion exchange liquid chromatography was employed for quantitatively resolving WSOC into the following main chemical classes: neutral compounds (N), mono- and di-acids (MDA) and polyacids (PA), the latter including humic-like substances. Proton Nuclear Magnetic Resonance ($^1\text{H-NMR}$) spectroscopy in D_2O solution was exploited for functional group characterization of WSOC.

Results indicate that laboratory-generated SOA are mainly formed by polar (water-soluble) organic compounds but also contain water-insoluble compounds. The water-soluble fraction is accounted for by mostly neutral compounds and monocarboxylic acids with a much lower contribution from dicarboxylic acids and HULIS. The $^1\text{H-NMR}$ spectra of α -pinene SOA show sharp peaks from individual compounds, including well-known species such as pinic and pinonic acids, superimposed to a broad background signal attributable to a more complex mixture of degradation products. Interestingly, the background signal increases with respect to the peaks of pinic and pinonic acids when low concentrations of the precursor VOC are employed in the chamber. Under such conditions, the $^1\text{H-NMR}$ spectra of α -pinene SOA show the best fit with those of SOA components isolated from ambient samples.

Quantification of Organic Functional Groups and Inorganic Compounds in Ambient Aerosols and Determination of Sources using Attenuated Total Reflectance FTIR Spectroscopy and Multivariate Chemometric Techniques at a rural site in Arizona

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An Attenuated Total Reflectance-Fourier Transform Infrared (ATR-FTIR) spectroscopic technique and a multivariate calibration method were developed to quantify organic functional groups and inorganic ions. Common aerosol functional groups such as aliphatic and aromatic CH, methylene, methyl, alkene, aldehydes/ketones, carboxylic acids, and common inorganic species, ammonium sulfate and ammonium nitrate as well as difficult to measure functional groups such as esters/lactones, acid anhydrides, carbohydrate hydroxyl and ethers, amino acids, and amines were quantified. Comparison of the sum of the mass measured by the ATR-FTIR technique and gravimetric mass indicate that this method can quantify nearly all of the aerosol mass on sub-micrometer size-segregated samples.

The method was applied to size segregated samples collected at Tonto National Monument, the IMPROVE sampling site for a federally mandated Class I area near Phoenix, Arizona. Additional samples were collected in downtown Phoenix and at an urban fringe site for comparison. On average, 39% of the PM_{1.0} mass at Tonto National Monument was composed of organic aerosol. The organic aerosol was composed of 34% (6%) biogenic functional groups, 21% (5%) oxygenated functional groups and 45% (7%) hydrocarbons.

Compositional analysis, functional group correlations, and back trajectories were used to identify three sources during the sampling period: biogenic, urban and regional background sources. The biogenic source had high concentrations of amino acids and carbohydrate hydroxyl and ether, as well as unsaturated hydrocarbons and qualitatively high levels of silicate and occurred when there was road construction near the site. The urban influenced sampling days had back trajectories coming directly from Phoenix and had high concentrations of hydrocarbons, oxygenated functional groups and nitrate. This aerosol characterization suggests that the secondary formation of aerosols from primary emissions in Phoenix had a major impact on the aerosol composition and concentration when air passes over Phoenix before arriving at TNM. The regional background source had low concentrations of all functional groups but had higher concentrations of biogenic functional groups than the urban source.

Effects of Post-Sampling Filter Treatments on the Measurement of Ambient Carbon Aerosols

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The mass of ambient carbonaceous particulate matter collected on quartz filters are prone to measurement error due to exposure to post-sampling field latency, shipping, and storage conditions. In 17 sampling events over a one year period, ambient PM_{2.5} aerosols were collected on quartz filters and subjected to various filter treatments which simulated a range of possible post-sampling conditions. The simulations included: mild heating at 40°C for hours or days, 48 hours of storage at -16°C and 48 hours of storage at room temperature (~21°C). The carbon mass on filters analyzed immediately after sampling and those analyzed after the filter treatments are compared to assess the potential and extent of measurement error due to the filter treatments.

Carbon mass on the filters was determined by thermal optical analysis using the IMPROVE_A Method temperature protocol implemented with a Sunset Analyzer. The mass of total carbon (TC), total organic carbon (TOC), total elemental carbon (TEC) and carbon fractions (OC1, OC2, OC3, OC4, OP, EC1, EC2 and EC3) were obtained. For each carbon fraction, the change in mass between the filters analyzed immediately after sampling and the treated filters were statistically classified using Analysis of Variance (ANOVA) and Tukey's Honestly Significant Differences multiple comparison procedure.

TOC and TC exhibited significant mass loss ($15\pm4\%$ and $10\pm4\%$, respectively) for filters heated for 96 hours but did not change for the frozen filters. TEC did not change for all filter treatments employed. OC1 always decreased due to heating – on average $22\pm7\%$ after being heated only six hours and $70\pm7\%$ after being heated for 96 hours and even decreased by $16\pm12\%$ after being stored at room temperature for 48 hours. OC2 decreased by on average $12\pm9\%$ for filters heated for 96 hours.

Filters collected by the IMPROVE network remain in the field up to seven days post-sampling and are shipped at ambient temperatures. We conclude that for IMPROVE carbon measurements and other samples handled in a similar way, OC1 is not a stable measurement.

DETERMINATION OF POLYCYCLIC AROMATIC HYDROCARBONS, N-ALKANES, HOPANES AND STERANES IN PM_{2.5} IN GOLDEN, CANADA BY THERMAL DESORPTION GC-MS

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Aerosol particulate matter with size less than 2.5 μ m (PM_{2.5}) has a large adverse effect on human health due to its small size and the many toxic organic compounds associated with the particles. Particulate matter levels in Golden, BC are among the highest in B.C. communities, and organic species comprise a significant portion of PM_{2.5}. A source apportionment study conducted by the University of Toronto, British Columbia Ministry of Environment and Environment Canada was completed in 2007. Analysis of chemical components included PM_{2.5} mass, trace metals, water-extractable anions and cations, organic carbon and elemental carbon and volatile organic compound. But few data were available on the chemical composition of the organic fraction of fine particles in Golden. In this presentation we report the concentrations and distributions of 16 PAHs, normal alkanes (C₁₀-C₄₀), 6 hopanes and 6 steranes in Golden particulate samples using direct thermal desorption-gas chromatography/mass spectrometry (TD-GC/MS) which overcomes some of the disadvantages of traditional solvent extraction methods.

All samples in this study were collected at the downtown site in Golden, British Columbia (B.C.), using a one-in-three day schedule from March 2006 to March 2007. Integrated twenty-four hour samples were collected on a 47mm quartz fiber filters and shipped back to the laboratory for chemical analysis. A single punch (8.1 mm diameter, 0.518 cm² in size) cut from the sample filter using a stainless steel round punch over a clean glass dish and loaded into the thermal desorption (TD) glass tube. The internal standards were also spiked onto the filter punch. During the analysis, the sample inside the TD tube was thermally desorbed to 320°C at a rate of 25°C/min. Desorbed analytes passed through a very short, heated (325°C) transfer line and were trapped on a packed glass wool liner in a cryogenically cooled injection system (CIS) whose initial temperature was kept at -60°C using liquid nitrogen. The CIS was then ballistically heated (720°C/min) to 325°C, which transferred the analytes in plug form to a DB-5 GC capillary column (0.25-mm i.d, 30-m length, 0.25- μ m thickness). The GC oven temperature was 60°C when the injection started, held isothermal for 3 minutes, followed by a temperature ramp of 5°C/min up to 320°C, with another isothermal hold for 10 minutes.

Individual organic species were found in each of 115 samples. The ambient concentrations of the total n-alkanes (C₁₀-C₄₀) in each sample during the collection period are in the range of 4.89-74.38 ng/m³, total PAHs (16 PAHs) 0.27-100.24 ng/m³, and total biomarkers (6 hopanes and 6 steranes) 0.14-4.39 ng/m³. N-alkanes constitute 33-98% of the total yield (sum of all organic compounds identified), 1-65% for PAH, and 1-8% for biomarkers. The annual means of the 16 PAH compounds range from 0.02 to 1.83 ng/m³, 0.07 to 1.55 ng/m³ for n-alkane compounds, and 0.02 to 0.18 ng/m³ for biomarkers. The annual sum of PAH from 1.83 (Fluorene) to 164.38 ng/m³ (Indeno[1,2,3-cd]pyrene), from 6.49 (Octatriacontane) to 137.08 ng/m³ (n Pentatriacontane) for n-alkane, and from 2.16 ($\alpha\alpha\alpha$ 20S-Cholestane) to 16.42 ng/m³ (17 α (H),21 β (H)-Hopane) for biomarkers. Seasonal trend and potential sources will be discussed in the presentation. Correlations of these molecular markers with organic carbon and elemental carbon will also be discussed.

**PRELIMINARY RESULTS ON APPLICATION OF OC/EC THERMAL
ANALYZER FOR THE ANALYSIS OF WATER EXTRACTABLE
ATMOSPHERIC HUMIC-LIKE SUBSTANCES IN PM_{2.5} SAMPLES FROM
SELECTED SITES IN CANADA**

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Carbonaceous species, organic carbon (OC) and elemental carbon (EC), constitute a major, sometimes dominant, fraction of fine particulate matter (PM_{2.5}). Organic carbon represents a large variety of organic compounds. Hundreds of non- or semi-polar organic compounds have been quantified using gas chromatography-mass spectrometry (GC-MS), however much less information is available on the water-soluble organic compounds (WSOC) including high-molecular-weight compounds, often named HULIS (humic-like substances).

Over the past few years several research groups have proposed different strategies to characterize WSOC and HULIS. This presentation reports on the use of thermal-optical carbon analyzer (DRI Model 2001) to determine levels and variations of WSOC and in PM_{2.5} samples collected on quartz fibre filters at 4 selected stations within the Canadian National Air Pollution Surveillance (NAPS) PM_{2.5} Speciation Program. A total of 40 samples selected from both winter and summer seasons were analyzed. A solid phase extraction cartridges (Oasis HLB, Waters) were used to isolate HULIS from aqueous extracts acidified to pH 2, followed by subsequent elution with methanol.

The estimated HULIS contributions to WSOC varied from low level (~26%) to high level (~72%) implying that HULIS do not share common origin and formation paths in different environments and seasons. Their average molecular weight estimated by LC-MS varied from ~290 to 350 and from ~270 to 420. The concentration of HULIS in summer correlated significantly with oxalic acid, a compound largely formed in secondary processes in the atmosphere, which suggests that higher photochemical activity promotes a higher concentration of HULIS in the particles. Preliminary results show that the combination of aqueous extraction, solid-phase extraction and thermal-optical carbon analysis is advantageous for studying the concentration and properties of HULIS in ambient PM_{2.5} samples

Measurements of the ratio of Aerosol Black Carbon (BC) to CO₂ in an Urban Basin as an indicator of Dispersed-Source Combustion Efficiency

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Keywords: BC, CO₂, global warming, emission factor

Aerosol black carbon (BC) is a ubiquitous pollutant species produced by the incomplete combustion of carbonaceous materials such as diesel fuel, biomass, and solid fuels. It creates impacts on public health, atmospheric radiative transfer and climate forcing. Atmospheric column optical depths greater than 0.5 are routinely observed over large areas of Asia, and the global warming effect of BC is second only to that of CO₂.

We measured black carbon and CO₂ concentrations in Ljubljana, a city of approximately 300,000 inhabitants. The urban atmosphere is impacted by traffic during rush hour (appr. 400,000 cars per day), two power plants burning gas and coal, combustion for residential heating, and other human activities. The city is located in a basin and experiences frequent temperature inversions with fog during winter. During these episodes, aerosol concentrations become high.

Data were collected from January to March 2008 at the urban monitoring site of the Environmental Agency of the Republic of Slovenia. We measured black carbon with an Aethalometer (Magee Scientific model AE42), and carbon dioxide with an electrochemical probe (Vaisala model GMP343). We studied the relationship between changes in aerosol black carbon and CO₂ during stagnation episodes. BC aerosol is an indicator of incomplete combustion, while increases in CO₂ represent the atmospheric inputs from the majority of the fuel carbon (method of Hansen et al., 1989). In each episode of increasing concentrations, we calculate the ratio between incremental BC and CO₂: $\Delta BC / \Delta CO_2$

Stagnation events with increases in concentration of BC and CO₂ were identified by wind speed, air temperature and temperature inversion. Table 1 shows results for three episodes with strong correlations between ΔBC and ΔCO_2 .

Figures 1 and 2 show very similar BC/CO₂ correlations for workdays and weekends of the entire data-gathering period.

This method of studying the ratio of increases of combustion effluent species concentrations, offers a technique to identify the emission characteristics of the dominant sources under real-world conditions.

Episode	Wind sp.	Temp	Events	Mass ratio (µg/g _{CO2})	
				workday	weekend
A	< 2 m/s	< 5°C		210	211
B	< 2 m/s	> 5°C		104	186
C	< 2 m/s	< 5°C	fog	102	239

Table 1: $\Delta BC / \Delta CO_2$ ratio in three episodes

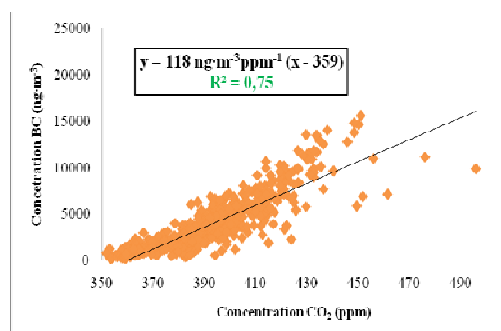


Figure 1: BC vs. CO₂ during workdays, winter 2008

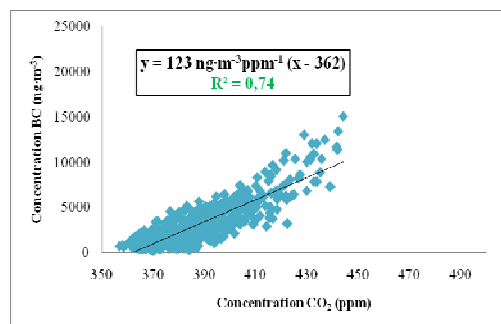


Figure 2: BC vs. CO₂ during weekends, winter 2008

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Extreme Black Carbon Snow Concentrations from a Chinese Glacier

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The deposition of black carbon (BC) to alpine glaciers decreases surface albedo and may accelerate glacier melt and retreat associated with temperature rise. Here we report extreme BC concentrations from snow pit and ice core samples taken from Glacier No.1 in the Tianshan Mountains of Northwest China. This glacier has rapidly retreated since the late 1980's in parallel with rising temperatures. During 2002 and 2006 snow pit samples for BC were collected from Glacier No. 1 and No. 51 as part of a multiyear snow pack process study (PGPI) undertaken by the Tianshan Glaciological Station, CAS. BC concentrations ranged from over 1 ppm to less than 20 ppb. The highest concentrations appear to be associated with super-imposed ice and likely result from post-depositional processes rather than wet and dry deposition. Mean BC concentrations of 250 ppb and 150 ppb were found for the 2002 and 2006 samples. In comparison mean BC concentrations of ~ 40 ppb were determined for the remote Glacier No. 51 in 2002. Ice core samples reveal that BC concentrations in the glacier have increased by up to 5 times during the latter half of the 20th century and likely result from emissions from of a coal-fired power plant in the Urumqi River valley ~ 20 km from the glacier. BC concentrations prior to the rise were comparable to modern snow at Glacier no, 51 samples suggesting little change in background concentrations during the 20th Century.

ON THE DEPENDENCE OF ARCTIC LIGHT ABSORPTION COEFFICIENT AND EQUIVALENT BLACK CARBON ON AEROSOL ORIGIN AND STATE OF MIXING

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Light absorbing black carbon (BC) in atmospheric aerosol appears to play a critical role in the global balance of radiative forcing and climate change. The concentration of major aerosol species such as sulphate and black carbon have shown a pronounced annual cycle with a winter-spring maximum and a summer-autumn minimum. The temporal variation of BC concentration in the arctic may be critical for accurate calculations in climate forcing models. Due to the absence of emission sources in the area and the episodic nature of the concentrations observed it is possible that the state of mixing of black carbon with other species and the degree of aging experienced by aerosol particles may be highly variable. Long term monitoring data obtained by means of an aethalometer are analysed in order to test certain corrections employed in the derivation of the absorption coefficient. The data obtained at seven wavelengths are also analysed for the interpretation of the observed variability across the optical spectrum in terms of aerosol origin or state of mixing.

Ambient measurements of BC concentration were obtained by means of a Magee Sci. AE-31 aethalometer operating at the Zeppelinfjellet station (474 m asl; 78°54'N, 11°53'E), Ny Ålesund, Svalbard. The concentrations recorded at a wavelength of 880 nm (Eleftheriadis and Nyeki, 2004) are considered to represent the concentrations of BC recorded by previous aethalometer models. Measurements are also converted by the methodology proposed by Arnott et al., (2005) to absorption coefficients for the wavelengths recorded at 30 min resolution. The scattering coefficients monitored at the same site by a three wavelength TSI Integrated Nephelometer are also incorporated in the absorption coefficient derivation algorithm.

Results for the 3-year period since 2001 indicate summer and winter average absorption coefficients of $0.06 \pm 0.10 \text{ Mm}^{-1}$ and $0.51 \pm 0.48 \text{ Mm}^{-1}$ respectively at 520 nm. A detailed analysis of the variability observed in the wavelength dependence and possible association with air mass origin was also conducted.

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CHARACTERISTICS OF ORGANIC TRACERS FOR BIOMASS BURNING ON A SUBTROPICAL ISLAND

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Biomass burning is a major source of carbonaceous aerosol particles on a global basis. The Asian continent is a particularly important source region for biomass smoke aerosol. Common biomass burning practices in Asia include a variety of combustion processes, such as domestic biofuel use and burning of agricultural residues. In the case of Taiwan, a subtropical island in East Asia, post-harvest burning of rice fields is the primary source of biomass smoke, strongly impacting local air quality during two burning seasons each year. In addition, transport of smoke aerosol to Taiwan associated with the outflow from the Asian continent may affect local air quality at times, while some small-scale burning of miscellaneous types of agricultural waste is observed at various times and locations throughout the year. The unique island setting of Taiwan may be particularly suitable for the assessment of local versus regional biomass smoke contributions.

This study assessed the impact of agricultural burning activities on a local scale by investigating the size-resolved distributions of anhydrosugars, including levoglucosan, mannosan and galactosan. These compounds are derived from the thermal breakdown of cellulose and hemicelluloses, and have been widely used as biomass burning source tracers. Ambient aerosol particles were collected before, during and after an episode of intensive rice straw burning at a rural and suburban site in south-central Taiwan. Polar organic aerosol constituents, including the anhydrosugars, were quantified by high-performance anion exchange chromatography (HPAEC) with pulsed amperometric detection (PAD).

While substantially increased biomass smoke tracer concentrations were observed during an active episode of rice straw burning (with ambient concentrations up to 1400 ng m^{-3}), fairly high values of the smoke tracers were measured throughout the entire post-harvest burning season of rice straw in Taiwan. Interestingly, a rather high mass fraction of the smoke tracers was present in aerosol particles with aerodynamic diameters larger than $10 \mu\text{m}$ ($\text{PM}_{>10}$), possibly influenced by the atmospheric conditions, such as high relative humidity, in addition to unique properties of rice straw smoke and the specific burning practices of rice fields. Furthermore, ratios of the individual anhydrosugars showed a different pattern from those in smoke aerosol generated by other types of biomass, such as wood, grass or other agricultural crops. Such chemical finger print could possibly be used in future source apportionment studies to obtain a first estimate regarding specific source types. In conclusion, this study has shown that unique conditions associated with burning practices in subtropical regions of Asia may give rise to distinctly different chemical and physical characteristics of the resulting smoke aerosol. Therefore, it is crucial for future research to better characterize biomass burning emissions and to generate source profiles which are representative of actual burning practices as well as the associated ambient conditions.

SECONDARY ORGANIC AEROSOL FORMATION FROM REACTIONS OF TERTIARY AMINES WITH NITRATE RADICAL

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Recent work has shown that reactions of amines with the nitrate radical lead to the formation of significant amount of aerosol.

In this study, secondary organic aerosol (SOA) formation from reactions of tertiary amines with nitrate radical was investigated using an aerosol mass spectrometer (AMS) and a proton transfer reaction mass spectrometer (PTR-MS). Three tertiary amines were reacted; Trimethylamine (TMA), Triethylamine (TEA) and Tributylamine (TBA). Results indicate that TBA forms the largest amount of aerosol mass followed by TMA and TEA respectively. Mass spectra from the AMS point to complex non-salt aerosol products, likely hydroxy amides. We propose a mechanism that proceeds via abstraction of a proton by the nitrate radical followed by RO_2 chemistry. Rearrangement of the aminyl alkoxy radical through H-shift leads to the formation of aerosol products.

These experiments show that night-time oxidation of tertiary amines by the nitrate radical can be an important source of SOA in regions with high mixing ratios of these species.

DISCERNING PRIMARY AND SECONDARY ORGANICS IN MARINE AEROSOL PARTICLES.

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We show the main chemical features of the marine organic aerosol and we illustrate how primary and secondary components can be distinguished by means of chemical properties based on the very recent results obtained in the three experiments carried out during 2006 in the framework of the EC project MAP.

The results of bubble mediated experiments during phytoplankton bloom revealed that organic carbon nascent spray particles exhibited a progressive increase in the organic matter (OM) content from $3 \pm 0.4 \%$ up to $77 \pm 5 \%$ with decreasing particle size, the rest being sea salt. Submicron OM was almost entirely water insoluble (WIOM): up to $96 \pm 2 \%$ in the 0.125-0.25 micro-meter size range. ^1H NMR analysis shows that WIOM in nascent marine aerosol forms from aggregation of lipo-polysaccharides exuded by phytoplankton. Colloids and aggregates are responsible for the decrease of surface tension observed in the aerosol water extracts. Our observations indicate that size dependent transfer of sea water organic material to primary marine particles is mainly controlled by the solubility and surface tension properties of marine OM.

These results indicate that organic insoluble carbon in marine aerosol can mainly be associated to primary production mechanisms and, as a direct consequence of this observation, the water soluble fraction (WSOM) is mainly accounted for by secondary organic aerosol formation processes. This fact is also evident from the ^1H HNMR analysis of WSOM fraction samples collected in clean sectors: the organic composition is always dominated by S-MSA signals and by two organic N species (mainly amines) and oxygenated species (mainly carboxylic acids and sugars). These findings also have potential implications for the atmospheric chemistry of aerosol particles and clouds.

EVALUATION OF THE WAVE-BREAKING ZONE INFLUENCE ON MARINE AEROSOL PHYSICO-CHEMICAL PROPERTIES.

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Marine aerosol physical and chemical properties were measured at Mace Head Research Station (coastal site) and on board the oceanographic vessel Celtic Explorer (open ocean site) sailing the North Atlantic off the Irish west coast, from 11 June to 6 July 2006. The campaign was held under the frame of the EU Project MAP (Marine Aerosol Production).

The size segregated chemical composition of organic and inorganic components were compared for coastal and open ocean aerosols to assess the potential influence of the coastal environment (wave-breaking zone) on marine aerosols advected over the continent from the open ocean.

Main chemical components (non-sea-salt sulphate, water soluble organic carbon, water insoluble organic carbon, ammonium, nitrate and sea salt) showed generally the same mass size distributions in the two datasets, resulting in a very similar average chemical composition for open ocean and coastal aerosol samples. Main differences were observed for primary marine aerosol components (sea salt and water insoluble organics) which showed comparable concentrations in the fine size fraction between coastal and open ocean samples but higher concentrations at the coastal site in the coarse size fraction.

The slightly higher contribution of water insoluble organic matter (WIOM) to total analyzed submicron mass registered over the open ocean addresses to a source of fine primary organic aerosol spread over the whole oceanic surface and not limited to the surf zone.

Characterization of water soluble organics performed by ^1H NMR showed many similarities between coastal and open ocean aerosol samples, addressing the same origin and removal processes.

The chemical characterization also evidenced aerosol processing during the transport from the open ocean to the coastal site: coastal samples presented lower $\text{MSA}/\text{nssSO}_4^{-2}$ ratio indicating possible oxidation process from reduced sulphur species to SO_4^{-2} . In the coastal samples we also observed a higher degree of oxidation of water soluble organics, which can also be an indication of ongoing organic oxidation processes.

The experiment showed that the advection over the coastal environment does not change the main marine aerosol physico-chemical properties in the submicron size range. The differences observed in the coarse fraction are, instead, likely due to the effect of the shoreline, enhancing coarse spray particles production.

EVALUATION OF PM_{2.5} ORGANIC CARBON SAMPLING ARTIFACTS: COMPARISON OF DATA FROM IMPACTORS AND QUARTZ FIBER FILTERS

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Particulate matter (PM) differs from other criteria pollutants in that it consists of a complex chemical mixture. Particulate organic carbon (POC) is a major contributor to PM and consists of thousands of individual compounds covering a full range of chemical and physical characteristics. Many POC constituents are found in significant fractions in both the gas and particulate phases. The amount in each phase depends largely on volatility and polarity. When PM is collected on a quartz fiber filter for bulk analysis by thermal volatilization methods, POC may volatilize once collected, or gaseous components may adsorb to either the filtration medium or previously collected particulate matter and therefore become apparent POC. These processes, known as collection artifacts, therefore, may cause a positive or negative measurement biases compared with the actual concentration found in the air at the time of collection. The objective of this research was to characterize the magnitude of these collection artifacts when sampling ambient air.

The approach was to simultaneously collect POC using both quartz filters and cascade impactors. The sampling methods used were: (1) a quartz-quartz filter pack (2) a Teflon-quartz-quartz filter pack, (3) an impactor with aluminum substrates to remove particles greater than 0.05 μ m diameter followed by a quartz-quartz filter pack and (4) a Teflon filter followed by a cascade impactor, followed by a quartz-quartz filter pack. Collection substrates were analyzed for organic and elemental carbon (OC and EC) using a thermal volatilization approach.

A significant and similar amount of OC was found on all final quartz filters regardless of whether particulate matter was first removed with a quartz filter, Teflon filter, or impactor. When particulate matter was removed with a Teflon filter, the OC on the following quartz filter was nearly twice that of a quartz filter in which the particulate matter was used to remove the particulate matter. The origin of this OC was therefore hypothesized to be the result of the quartz back filter collecting volatile organic carbon (VOC). The amount of POC on a quartz filter should therefore be calculated by subtracting the positive VOC adsorption artifact from the OC on the filter. This artifact is best estimated by the amount of OC on the quartz filter following a Teflon filter.

Applying this correction to OC on both a front quartz filter (#1) and an impactor-filter combination (#3) resulted in nearly equal amount of POC. Since the impactor stages collected most of the particulate matter and little VOC, the correction for the after-filter is quite large, approximately 90% of the OC on this filter is an adsorption artifact. Given this large correction, sampling with quartz filters alone is preferred if a particle-size distribution is not needed. The good comparability between the two sampling approaches gives a strong indication that the collection artifact is due to adsorption of VOC by quartz filters and not volatilization of collected particulate matter followed by capture on the quartz filter. If the latter were significant, more volatilization would be expected from a front quartz filter than from impaction substrates in which the particles collected are almost immediately covered with other particles.

SNOW-ALBEDO FEEDBACK TRIGGERED BY CARBONACEOUS PARTICLES

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Nearly all atmospheric aerosol mixtures exert a positive radiative forcing over snow, because of its high reflectance. This forcing becomes even larger when considering the darkening effect of deposited particles. Here, we apply a column radiative transfer model to show that surface darkening from carbonaceous particles also exceeds the competing influence of "dimming" caused by atmospheric constituents, resulting in a net positive surface forcing over snow. Consequently, studies with global climate models indicate that emissions of black and organic carbon trigger strong snow-albedo feedback during boreal spring, when a large portion of the Northern Hemisphere is snow-covered and exposed to intense insolation. Accordingly, climate forcing caused by darkened snow has greater efficacy than any other anthropogenic mechanism. We also explore this forcing in the context of accelerated springtime warming and snow cover depletion over Eurasia, where black carbon emissions have been rising.

SIZE-SEGREGATED ABSORPTION MEASUREMENTS OF TRAFFIC AND URBAN BACKGROUND AEROSOL

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Traffic is a significant emission source of fine particulate matter (aerodynamic diameter D_a below $2.5\ \mu\text{m}$, $\text{PM}_{2.5}$) in urban and urban background areas. Soot is one of the most abundant components in vehicle emissions. Especially, the number concentration of ultrafine ($D_a < 100\text{nm}$) soot particles in the areas influenced by the traffic can be significant (Rose et al., 2005). Ultrafine particles including soot play an important role in aerosol-induced health effects (Ibald-Mulli et al., 2002). In addition, soot is the most efficient particulate light absorber. Thus, it has an effect to global radiative balance. When the optical methods are used to analyze absorbing part of the fine particles, soot is often called black carbon (BC). In this study, BC levels of urban background and traffic aerosol were investigated using instrumentation measuring the light absorption by particles.

The measurements were done in Helsinki, Finland, at an urban background station SMEAR III ($60^{\circ}20'\text{N}$, $24^{\circ}97'\text{E}$, 26m above sea level) and in a mobile laboratory Sniffer (Pirjola et al., 2006) inside traffic. The latter measurements were done during evening and morning vehicular rush-hour period in the city centre and in the heavily trafficked ring roads in Helsinki. Absorption coefficients σ_{AP} were measured using two 3-wavelength Particle Soot Absorption Photometers (3λ PSAP, Radiance Research, Seattle, WA, USA, Virkkula et al., 2005) which were equipped with a size-preselector with the cut-off diameters $1\ \mu\text{m}$ and $0.170\ \mu\text{m}$, respectively. In addition, a 3-wavelength nephelometer (TSI model 3563, St Paul, MN, USA) was used to detect scattering coefficients σ_{SP} for the iterative correction procedure of PSAP data as presented by Virkkula et al. (2005). The particle size classification of BC particles was based on the differences between absorption from the two PSAPs with different cut-off diameters. The analyzed dataset includes continuous measurement period at the SMEAR III station between June 12 2007 and end of January 2008. Inside traffic measurements were done December 13-14, 2007. Particle number size distribution ($7\ \text{nm} - 10\ \mu\text{m}$) was measured by an Electrical Low Pressure Impactor (ELPI, Dekati Ltd.).

At the SMEAR III station, the investigation showed clear seasonal differences in the ratio of σ_{AP} (wavelength $\lambda=660\ \text{nm}$) for two different size ranges. σ_{AP} with cut-off diameter $0.170\ \mu\text{m}$ ($\sigma_{\text{AP},0.170\mu\text{m}}$) was on average (\pm std) $53 \pm 26\%$ from the σ_{AP} values with $1\ \mu\text{m}$ cut-off ($\sigma_{\text{AP},1\mu\text{m}}$). From June to October, the fraction of $\sigma_{\text{AP},0.170\mu\text{m}}$ from $\sigma_{\text{AP},1.0\mu\text{m}}$ was on average $64 \pm 19\%$ whereas during December and January it was $25 \pm 18\%$. Vehicular rush-hours did not show clear increase of $\sigma_{\text{AP},0.170\mu\text{m}}$ fraction in relation to $\sigma_{\text{AP},1\mu\text{m}}$. This is most likely because of a high contribution of long-range transported aerosol in the urban background environment. The aim of the mobile laboratory measurements was to study the influence of freshly emitted particle emissions to the fraction of the lower cut-off BC ($\sigma_{\text{AP},0.170\mu\text{m}}$). The $\sigma_{\text{AP},0.170\mu\text{m}}$ -to- $\sigma_{\text{AP},1.0\mu\text{m}}$ ratio was lower than the average value in urban background, 0.47 ± 0.15 and 0.36 ± 0.19 during morning and evening rush hours, respectively. One possible reason for that may be particle growth by semivolatile organic material immediately after the exhaust to the air.

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NEWLY DESIGNED BLACK CARBON MONITOR (COSMOS) AND ITS PERFORMANCE

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Abstract. We have newly designed a continuous soot monitoring system (COSMOS) for fully automated, high-sensitive, real time measurements by light absorption from black carbon (BC) aerosols. COSMOS measures the changes of transmittance across an automatically advancing quartz fiber filter tape using a LED with 565 nm wavelength. It uses a double-convex lens and optical bundle pipes to maintain high light intensity. Data signal is obtained with the sampling rate of 1,000Hz. These factors significantly improved sensitivity of the BC detection. In addition, sampling flow rate and temperature of the optical unit are actively controlled to achieve a stable and long-term operation. The inlet line is heated to 400 °C to effectively volatilize non-refractory aerosol components that are internally mixed with BC. From the measurements of background level of COSMOS, the detection limit was found to be better than 0.45 Mm^{-1} ($0.045 \mu\text{g m}^{-3}$) for 10-min measuring time. The reproducibility of BC measurements by different units of COSMOS was better than $\pm 1\%$ ($r^2=0.99$). The absorption coefficients determined by COSMOS agreed with those by a particle soot absorption photometer (PSAP) to within 1% ($r^2=0.97$), and the precision ($\pm 0.60 \text{ Mm}^{-1}$) for 10-min averaged data was better than those of PSAP and Aethalometer under our test conditions. The field measurements were also made at various locations comparing with the EC/OC analyzer and the other commercial instruments. These comparisons have demonstrated reliability of COSMOS for continuous measurement of BC mass concentrations in remote and urban areas. The design concept and the some of the performance data of this instrument will be shown in this conference.

BULK CHARACTERIZATION OF ORGANOSULFATES IN CONTINENTAL FINE AEROSOL

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Abstract

Organic aerosol is now a major constituent of tropospheric fine aerosol and its effects are becoming increasingly important in determining climatic and other effects of atmospheric aerosol. A significant fraction of organic aerosol is formed in the atmosphere as secondary organic aerosol (SOA). It has been shown quite recently that heterogeneous reactions involving acidic seed aerosol significantly enhance secondary organic aerosol (SOA) yields in controlled smog chamber experiments. Recent targeted mass spectrometric studies identified specific sulfate esters of abundant biogenic carbonyl compounds in both smog chamber and continental aerosol suggesting that behind the enhanced SOA yields organosulfate formation is involved. However, bulk characterization as well as quantification of this compound class have been lacking so far in most studies.

In this paper ultra-high resolution non-targeted approach using electrospray ion cyclotron resonance Fourier transform mass spectrometry (ESI-ICR-FT/MS) was used to characterize organosulfur compounds in water-soluble continental fine aerosols. The ubiquitous occurrence of such compounds, as well as the distribution of their elemental composition and molecular mass was established. The mass concentrations of total organic sulfur bulk were determined indirectly in size segregated water soluble aerosols by concurrent independent measurements of different sulfur species. Our results showed that the bulk mass of organosulfate species were significant even compared to sulfate. The inferred size distribution as well as elemental composition variations of bulk organosulfates in selected samples suggested that they possibly form in heterogeneous reactions of condensable semi-volatile carbonyl compounds and gaseous sulfuric acid on particle surfaces.

BLACK CARBONS, FRESH, AND AGED BIOMASS BURN PARTICULATES: EVIDENCE OF OXYGENATED INTERFACES

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Carbonaceous particles formed by combustion are the strongest absorbers of visible light out of any other particle type. Understanding and characterizing the diversity of particulate matter produced from fossil fuel and biomass burn combustion is important for determining the magnitude and sign of radiative forcing by aerosols. Scanning transmission x-ray spectroscopy with near edge x-ray absorption fine structure (NEXAFS) spectroscopy is used to explore the diversity of light absorbing particles. Information is presented on the percent of carbon involved in C=C double bonds (sp^2 hybridization) and total atomic carbon/oxygen ratios. Light absorbing aerosols studied include numerous laboratory surrogates, spherical aged biomass burn particulates (tar balls), particulates collected from laboratory burns of selected biomass fuels, and field samples collected in the recent MILAGRO study in Mexico City. For tar balls, a detailed examination of the carbonyl peak area (normalized to the total carbon) as a function of particle size indicates the presence of a thin oxygenated interface layer, which could enhance the particle absorption. NEXAFS spectra of tar balls indicate carbon bonding and carbon/oxygen ratios that are more similar to humic type substances and dissimilar to flame generated black carbon. From the laboratory biomass fuel burns, a wide range of particle types were observed. Some particulates were dominated by salts, others by fractal type soot, and a third particle type contained organic carbon with soot inclusions. Understanding the range of particulates formed from biomass burns and the differences compared to other light absorbing particulates is important for developing improved models of their radiative influence.

GLOBAL EMISSION INVENTORIES OF GASES AND PARTICLES FROM FOSSIL FUEL AND BIOFUEL CONSUMPTION FOR THE PERIOD 1860-2030 WITH TENTATIVE VALIDATIONS WITH CARBONACEOUS AEROSOL TM4 GLOBAL MODELING

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Emission inventories have been developed from fossil fuel and biofuel consumption for 1860 to 2030 using Junker and Liousse, 2008. The inventory for 1950 to 2003 is based on the United Nations Energy Statistics Database with two simplifications : a) fuels are categorized into three usage classes with associated emission factors (EF) (industrial, domestic and traffic). b) the different EF occurring in similar fuel/usage combinations as a consequence of the different technologies are categorized into three classes (industrialised, semi-developed and developing countries). Fossil fuel and biofuel consumptions for the period 1860-1949 are issued from Etemad et al., 1991 and Mitchell et al., 1995. The method for 1950-2003 was further simplified for the earlier period. The prospective inventory is based on energy consumption forecasts by the Prospective Outlook on Long-term Energy Systems (POLES) model (Criqui, 2001) for a reference scenario vs a "clean" one. Our inventories use EF variable in time for gases and particles. Spatial distributions of emissions are obtained in proportion to population densities. Emission budgets are shown and compared with previous existing inventories with a focus on their trends. Finally, these BC and OC inventories associated with biomass burning sources are implemented in the global TM4/ORISAM model. Global modeled BC distributions are displayed for 1900, 1950, 2000 and 2030, with tentative validations against ground measurements.

THERMAL SPECTRAL ANALYSIS

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Thermal optical analysis (TOA) is used to measure the carbon content of aerosol samples. Monochromatic (i.e., red laser) light transmitted through (or reflected by) the sample during thermal evolution is monitored to indicate the amount of char formed from the pyrolysis of organic carbon (OC) and to aid in differentiating between OC and black carbon (BC). The quantification of BC is, nonetheless, very uncertain for samples that char.

A potentially beneficial enhancement to current TOA methods involves monitoring samples over a broad spectral region instead of at a single wavelength. The benefits of “thermal spectral analysis” (TSA) include (1) quantification of the absorption Ångström exponent of the aerosol sample, (2) improved characterization of the optical properties of char, and (3) improved estimates of the sample BC content. We equipped the carbon analyzer at Lawrence Berkeley Lab with a bright white light-emitting bulb and an optical spectrometer with a fixed grating and a linear CCD-array detector and analyzed a variety of laboratory-generated and field samples to demonstrate these benefits:

(1) Absorption Ångström exponent: Comparing broadband (e.g., 400-1000 nm) transmission of the sample before and after thermal analysis yields the absorption Ångström exponent, a metric that has become popular with the recognition that organic carbon, particularly from biomass burning, absorbs light.

(2) Optical properties of char: The change in the absorption Ångström exponent with increasing sample temperature – the *absorption Ångström exponent thermogram* – in combination with the mass normalized *attenuation coefficient thermogram* provides a quantitative optical characterization of the sample throughout its analysis, including the pyrolyzed OC (i.e., the char). Thermograms are presented for laboratory samples of flame-generated BC, secondary organic aerosols (initially non light-absorbing OC that charred), smoldering cellulose (light-absorbing OC that charred) and mixtures of OC and BC (including motor vehicle and biomass burning aerosols).

(3) Improved BC quantification: The TSA method was applied to filtered precipitation samples. Since these samples charred and the char co-evolved with BC, an algorithm was developed to aid in quantifying BC. BC and charred organics are distinguished by differences in their light absorption selectivity. The transmission of light through the filter can, therefore, be separated into two signals: that of charring organics and the original BC in the sample, which may then be converted to mass concentration of both BC and char using individual mass attenuation efficiency values. Simultaneous measurements of evolved carbon, as CO₂, constrain and validate the final result.

A CASE ANALYSIS OF SUBMICRON ORGANIC AEROSOL MASS SPECTRA DURING SPRING OF 2008 AT TSUKUBA IN JAPAN

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Recent case studies of submicron organic aerosols have resulted from the application of the Aerosol Mass Spectrometer (AMS) that can determine quantitatively organic aerosols with high time and size resolution. Since High Resolution Time of Flight AMS (HR-ToF-AMS) has been developed, the high mass resolution allows the separation of each unit mass peak into separate contributions for specific elemental compositions based on small differences in mass defect. The high resolution of the HR-ToF-AMS has already been demonstrated in the some field studies and will provide valuable insight into the elemental composition of organic-containing particulate matter.

Here we will report initial results of Japanese field measurement by ToF-AMS during the spring of 2008 at Tsukuba (36°04'N, 140°04'E) where located at semi-rural site of the Kanto plains, and it will be discussed the time variations for accurate mass spectra signals and positive matrix factorization analysis compared with other air pollutants matter.

CHANGING NATURAL-ANTHROPOGENIC AEROSOL MIXTURE OVER NORTHERN EUROPE AND ITS POSSIBLE EFFECT ON REGIONAL CLIMATE

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The aerosol effect on the radiative balance of the atmosphere is believed to be substantial, and changes in particle emissions could have a considerable impact on earth's climate. The aerosol concentration is controlled by both natural and anthropogenic sources. Recent studies have clearly indicated that it is necessary to understand how different sources contribute to the aerosol and how these sources will change due to both policy making and climate change.

The most important natural organic carbon emitter in the northern hemisphere is the boreal forest. For the Scandinavian region, it has been shown that natural biogenic emissions of monoterpenes ($C_{10}H_{16}$) dominate VOC concentrations (Simpson et al., 1999). It was further shown in Tunved et al. (2006) that temperature dependent emissions of aerosol precursors largely control the aerosol evolution in clean air masses over the boreal forest. In a following study, Tunved et al. (2008) showed that the mass that the forest typically can support somewhere between 10-50% of the average mass observed in today's mixed natural-anthropogenic conditions of the Scandinavian region. This means that the forest is an important source of particulate matter, at high latitudes in Europe even comparable in magnitude with present anthropogenic emissions.

Since the particles formed from monoterpene oxidations products have been shown to be able to serve as Cloud Condensation Nuclei (CCN's, e.g. Hartz et al., 2005), the aerosol production over the forest may further be important for the radiation budget of the atmosphere. Since the emissions of terpeneoids are temperature dependent, increasing temperatures are likely to lead to increasing emissions from forests. This could possibly also alter the nature and concentration of the aerosol over and outside forested areas. Furthermore, since mid-80's, European sulfur emissions have decreased significantly. Being an excellent precursor for aerosol formation, decreasing SO_x emissions have had a large impact on the aerosol field over Europe. In principle, the changes in emissions of aerosol precursors induced by reduced anthropogenic emissions and increasing temperatures (BVOC emissions) will bring the aerosol towards a state where the natural, predominantly organic portion of the aerosol is likely to increase. Concurrent, the relative portion of the anthropogenic, inorganic species (i.e. sulfur) is likely to decrease.

In this study we have used a two layer box-model including a state-of-the-art aerosol dynamic model (UHMA, Korhonen et al., 2003) coupled with a chemical box-model and an adiabatic cloud parcel module to study the evolution of the aerosol as air-masses are transported to Scandinavia under different, typical, meteorological conditions using different emission scenarios. For this we have utilized available emission data of SO_x and other anthropogenic particle precursors (EMEP, MSCW) through years 1980-2003 combined with temperature dependent natural emissions of monoterpenes and sesqui-terpenes to study how the aerosol over Scandinavia is likely to have changed with changing emissions and, further, how the Scandinavian aerosol could respond to increasing emissions from the forest in times of changing climate.

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SIZE-RESOLVED CARBONACEOUS PARTICLES IN ROADSIDE AND AMBIENT ATMOSPHERE IN JAPAN

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Number concentration and size distribution were measured with Scanning Mobility Particle Sizers (SMPS, TSI) at several sites in and around Tokyo, Japan. The high number concentrations with bimodal size distribution with distinctive peak at 0.02-0.03 μm and small peak at 0.06-0.08 μm in diameter were observed in winter at roadside sites. The number concentrations at ambient atmosphere monitoring sites were much lower than those at the roadside sites, and the number size distribution at ambient atmosphere monitoring sites was monomodal with the peak diameter around 0.05-0.06 μm .

Size-resolved carbonaceous components in roadside and ambient atmosphere were also investigated. Particles were collected by low-pressure impactors (DLPI, Dekati; Nano-MOUDI II, MSP), and mass concentration of particulate matter (PM), elemental and organic carbons (EC and OC) were measured. The mass size distributions of PM showed three peaks around 0.1-0.2 μm , 0.5-1 μm and 5-8 μm in roadside atmosphere, whereas only one peak around 0.5-1 μm in ambient atmosphere. The mass size distributions of EC had sharp peak at around 0.1 μm in roadside atmosphere, whereas broad peak at around 0.4 μm in ambient atmosphere. Total carbon (TC) accounted for about 60-80% of PM at 0.03-0.29 μm in roadside atmosphere, whereas about 40-50% in ambient atmosphere. In addition, the ratio of EC to TC was distinctively higher around 0.1 μm in roadside atmosphere (70-80%) than in ambient atmosphere (50%). Considering these facts together with mass size distribution of diesel exhaust particles (DEP) with sharp peak around 0.1 μm , it is suggested that particles of 0.03-0.29 μm in roadside atmosphere are directly influenced by DEP. However, TC accounted for about 20% of PM and the ratio of EC to TC decreased to 20-40% at 0.01-0.03 μm , the peak diameter of number size distribution in roadside atmosphere. Interestingly, the number size distribution at a background site only 200m away from a roadside site has no peak around 0.02-0.03 μm . Organic analysis of the size-resolved particles at the roadside and background sites suggested that lubricating oil from vehicles affected the organic composition of both the roadside and background 0.03-0.06 μm particles, and that C₃₃ n-alkane and more volatile organic compounds in the 0.03-0.06 μm particles partially evaporated in the atmosphere after the emission from tailpipes of diesel vehicles. It is likely that evaporation of the constituents (or possibly coagulation with pre-existing particles after shrinking by partial evaporation) of nanoparticles in the atmosphere was responsible for the absence of nanoparticles in the background atmosphere.

Reference Fushimi, et al.: Atmospheric fate of nuclei-mode particles estimated from the number concentrations and chemical composition of particles measured at roadside and background sites. *Atmospheric Environment*, 42, 949-959, 2008.

ENHANCED SOA FORMATION DUE TO WATER UPTAKE BY FINE PARTICLES

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This study characterizes the partitioning behavior of a significant fraction of the ambient organic aerosol through simultaneous measurements of gas and particle water-soluble organic carbon (WSOC) in summertime Atlanta, Georgia. The partitioning of WSOC had no correlation with either temperature or particulate organic carbon mass concentrations, but did show a strong RH dependence that was attributed to aerosol liquid water. At elevated RH levels (> 69%), WSOC showed a significant increase in partitioning to the particle phase that followed the predicted water uptake by fine particles. The enhancement in particle-phase partitioning translated to increased median particle WSOC concentrations ranging from 0.3-0.9 $\mu\text{g C m}^{-3}$. The results provide a detailed overview of the WSOC partitioning behavior in the summertime in an urban region dominated by biogenic emissions, and indicate that secondary organic aerosol formation involving partitioning to liquid water may be a significant aerosol formation route that is generally not considered.

AN IN-SITU METHOD OF ORGANIC AEROSOL SPECIATION VIA THERMAL DESORPTION GAS CHROMATOGRAPHY-MASS SPECTROMETRY (TAG)

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Organic matter comprises 20-50% of the mass of airborne particles, yet information about its composition at the molecular level is limited. Hundreds to thousands of compounds identified through chromatographic mass spectrometry techniques. Although those identified comprise a fraction of the total organic mass, they serve as valuable tracers for sources of primary constituents, and provide valuable insights into the origin of secondary constituents. Presented here is the highly time-resolved measurement of these organic compounds through Thermal-desorption Aerosol Gas chromatography/mass spectrometry (TAG).

Our TAG instrument provides automated, hourly in-situ measurements of aerosol organic marker compounds. With TAG, particles in the size range from 0.1 to 2.5 μm are collected by means of humidification and impaction. Once each hour the sample is thermally desorbed and transferred to the head of a column for gas chromatography/mass spectrometry (GC/MS) analysis. This analysis proceeds during the collection of the subsequent sample. The system operates automatically, providing around-the-clock, hourly measurements. As part of the automated cycle a Teflon pre-filter is switched in-line to measure the dynamic field blank. Calibrations are done manually with liquid standards injected directly into the cell, and analyzed using the normal automated cycle. The TAG approach offers the advantage of building on past research using filter-based GC/MS analyses to quantify organic material and identify the origins and transformations of organic aerosols.

We present example hourly measurements of organic speciation of atmospheric aerosol from two California locations: an urban site in Riverside, and a remote site adjacent to the Blodgett Forest research station in the foothills of the Sierra Nevada Mountains. Measurements in Riverside were made in August and November, 2005 as part of the Study of Organic Aerosol at Riverside (SOAR). Measurements at the Blodgett site were made in a ponderosa pine plantation as part of the Biosphere Effects on AeRosols and Photochemistry EXperiment (BEARPEX) from September 9th – October 10th 2007 during the transition from the summer to fall seasons. We also present comparisons to quartz filters from NIST analyzed by TAG and by normal GC/MS methods.

During both studies the hourly time resolution of TAG provides far greater information on diurnal variations than more traditional filter samples. In Riverside we tracked the hourly profiles of more than 300 individual organic compounds over two, two-week periods. Factor analysis of these data shows contributions from anthropogenic particle sources such as vehicle emissions, meat cooking, biomass burning, pesticide use, herbicide use, along with primary biogenic sources such as plant emissions and plant waxes. The data indicate secondary organic aerosols formed as a result of the oxidation of biogenic and anthropogenic precursor gases.

At Blodgett we observe higher concentrations of anthropogenic marker compounds (e.g., phthalic and benzoic acids) in the early afternoon with the arrival of the pollution plume from Sacramento. While higher concentrations of biogenic marker compounds (e.g., pinonaldehyde and nopinone) are observed at night suggesting local oxidation of primary biogenic emissions in the shallow nocturnal boundary layer. Radiocarbon (carbon-14) analysis at the site shows that 70 – 100% of the carbon present in the PM_{2.5} aerosol is modern indicating the importance of biogenic sources on aerosol composition at this site. We use the TAG data in conjunction with aerosol mass spectrometer (AMS) measurements to investigate the relative contributions of different source categories (e.g., biomass burning, primary biogenic emissions, secondary biogenic oxidation etc) to aerosol composition during the BEARPEX campaign.

SINGLE-PARTICLE LASER-INDUCED FLUORESCENCE (LIF) SPECTRA OF ATMOSPHERIC AEROSOL: EFFECTS OF BRIEF HEATING

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We measured laser-induced fluorescence (LIF) spectra of single atmospheric aerosol particles, on-the-fly, with our particle fluorescence spectrometer (PFS), and analyzed the spectra using an unstructured hierarchical cluster analysis. Measurements were made at Adelphi, MD [1], and at New Haven, CT and Las Cruces, NM [2]. The threshold of the distance metric (dot product between any two normalized spectra) used in the cluster analysis was chosen so that a high fraction (typically around 90%) of the LIF spectra fall into 8 to 10 clusters. The measurements were taken at different times of year (spring, fall, winter) at sites with different regional climates (East seaboard of USA vs. Chihuahuan desert). Even with these differences, there are remarkable similarities among most of the primary clusters found at the three sites. The fraction of particles in each cluster, however, varies with time and regional climate. Fluorescent molecules in the atmosphere are almost exclusively organic carbon (OC) (including biological OC), and, in the great majority of cases are aromatic OC, e.g., polycyclic aromatic hydrocarbons (PAH), substituted and partially oxidized PAH, and heterocyclic aromatics such as tryptophan. Some of the clusters found at each site have spectra that are similar to spectra of some important classes of atmospheric aerosol, such as: a) bacteria and proteins (spectra dominated by tryptophan); b) marine aerosol; c) humic/fulvic materials, combustion aerosols and PAH, and humic-like substances (HULIS); and d) cellulose. On average, the broad spectra characteristic of some humic/fulvic acids, HULIS and some combustion aerosols comprise 28-43% of fluorescent particles at all three sites. Cellulose-like spectra contribute only 1-3%. Bacteria-like spectra comprise around 1-2% of the LIF spectra. To obtain a more information about the possible organic materials in the particles in the different clusters, we heated the particles by drawing the sampled air through a heated anodized aluminum tube prior to its entering the PFS. In measurements made at New Haven, CT, we found that the cluster with bacteria-like spectra appeared especially sensitive to temperature, although statistical variations prevent us from making a more definitive statement at present. The humic-HULIS-combustion-aerosol cluster is the least sensitive to high temperature, and in some cases does not decrease appreciably even at the highest temperature used (300 °C). This thermal stability is more consistent with PAHs and other combustion aerosols than it is with humic and fulvic substances. Large PAHs, e.g., benzpyrene, tend to be insensitive to temperatures of 300 °C. Compounds that withstand the high temperatures of combustion engines and do not quickly react, may be expected to withstand 300 °C in our heating tube. So, the high temperature studies are more consistent with the humic-HULIS-PAH cluster of atmospheric aerosol being dominated by combustion products, at least in New Haven in winter. Preliminary results with dual-wavelength excitation will also be described. We thank the Joint Services Technology Office for Chemical and Biological Defense for their support.

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MEASUREMENTS OF BLACK AND BROWN CARBON IN ATMOSPHERIC AEROSOLS WITH THE INTEGRATING SPHERE METHOD

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Until about a decade ago, black carbon (BC) was thought to be the only light absorbing substance in the atmospheric aerosol except for soil or desert dust. In more recent years, light absorbing polymeric carbonaceous material was found in atmospheric aerosols. Absorption increases appreciably towards short wavelengths, so this fraction was called brown carbon (e. g. Andreae and Gelencser, 2006). As brown carbon is thermally rather refractory, it influences the split between organic carbon (OC) and elemental carbon (EC) in thermal methods, and, through its light absorption characteristics, leads to overestimations of BC concentrations.

In this study, the integrating sphere method (Hitzenberger et al., 1996) was extended to correct the BC signal for the contribution of brown carbon and to obtain an estimate of brown carbon concentrations. In the original integrating sphere (IS) method, the attenuation signal of an aerosol sample is converted to BC concentration using a calibration curve obtained with a commercial carbon black. If the aerosol contains other light-absorbing material, however, this procedure leads to overestimated BC concentrations. The wavelength range of the IS was extended to enable also measurements at 402, 450, 550 and 650 nm. Using a second calibration curve obtained for a proxy of brown carbon (humic acid sodium salt) and an iterative method, the different wavelength dependence of the absorption signals led to corrected BC concentrations and also an estimate of brown carbon concentrations.

The extended method was first tested on mixtures of test substances and then applied to atmospheric samples collected during biomass smoke episodes (Easter bonfires) in Austria. The resulting concentrations of black and brown carbon are compared to EC obtained with a widely used thermal method, the Cachier method (Cachier et al., 1989) and a thermal-optical method (Schmid et al., 2001), as well as to concentrations of humic like substances (HULIS) and to biomass smoke POM (particulate organic matter). Both the thermal methods were found to overestimate BC on days with large contributions of woodsmoke. During the days of the bonfires, brown carbon was found to contribute 35 - 54% to biomass smoke POM, while HULIS accounted for 32 to 52% of brown carbon. During these days, the Cachier method gave EC concentrations that were higher by a factor of 3.79 than the BC concentrations, while the concentrations obtained with the thermal-optical method were higher by a factor of 2.63.

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TRENDS IN ATMOSPHERIC ELEMENTAL CARBON CONCENTRATIONS FROM 1835 TO 2007

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Elemental carbon (EC) aerosols absorb solar radiation which results in heating of the atmosphere. Recent increases in the atmospheric burden of EC may account for ~10 to 15 % of global warming. Long-term EC data, however, are sparse. We report here our measurements of annual mean atmospheric EC concentration, $[EC]_{atm}$, from filter samples collected daily from 1978 to 2005 at Whiteface Mountain, NY using the thermal optical method. The $[EC]_{atm}$ for 1978-86, 1987-96, and 1997-2007 were, 550, 225, and 72 ng m⁻³, respectively. We also collected ~ 55 cm long sediment cores from West Pine Pond near Whiteface Mountain. The cores were sliced and their ²¹⁰Pb ages determined. The first (top) five slices each represented sediment deposition over 7 y and the remaining 13 y each. EC was chemically separated from the sediment samples from four cores, and its concentration in each slice was determined using the thermal optical method. The $[EC]_{sed}$ followed closely that of $[EC]_{atm}$ from 1978 to 2005. Assuming wet and dry deposition as the only source, we can show that $[EC]_{sed} = K[EC]_{atm}$, where K (m³ g⁻¹) is a constant for a given lake. From $[EC]_{atm}$ and $[EC]_{sed}$ for the 1978-2005 period, K was determined to be 10,400 ± 4,400 m³ g⁻¹. With this value used for K and $[EC]_{sed}$, the $[EC]_{atm}$ values were determined from 1835 to 1978. The $[EC]_{atm}$ from 1835- 62 was ~30 ng m⁻³, which may be close to the pre-industrial background level. The $[EC]_{atm}$ was 65 ng m⁻³ for the 1863-75 period, then increased sharply, reaching a maximum value, 760 ng m⁻³, from 1917- 30. From 1931- 43 through 1978-84, the concentration decreased gradually, from 680 to 560 ng m⁻³. The concentrations for 1985-91, 1992-98, and 1999-2007 were 295, 195, and 60 ng m⁻³, respectively. Model calculations for BC emissions from fossil fuel combustion for the US by Novakov et al., [2003] qualitatively reproduce the trend determined experimentally in this work.

IDENTIFICATION OF CINEOLE OXIDATION PRODUCTS IN BIOGENIC SECONDARY ORGANIC AEROSOL

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Detailed organic speciation of summer time PM₁₀ collected in Melbourne, Australia was performed using HPLC/ESI-TOFMS (high-performance liquid chromatography simultaneously coupled to electrospray ionization time-of-flight mass spectrometry) and ESI/ITMSⁿ (electrospray ionization ion trap mass spectrometry). The obtained chromatograms show the presence of numerous monoterpene oxidation products from α -pinene and β -pinene. In addition, two polar oxygenated compounds with molecular formulae of C₉H₁₄O₆ and C₁₀H₁₆O₆ are detected at the higher levels during and after the period with an influence of a bushfire. In order to elucidate the origin and the structures of these compounds, a series of monoterpene oxidation experiments was conducted in an indoor aerosol chamber. The oxidation products from 1,8-cineole, which occurs in eucalyptus trees, show the same chromatographic and mass spectroscopic behaviors to the compounds detected in the ambient samples. The compound with a molecular formula of C₁₀H₁₆O₆ is further characterized by fragmentation experiments. Its fragmentation pattern shows a neutral loss of 60 u, suggesting the presence of an acetate ester with an open ring structure (Figure 1). The concentration of this compound is estimated to be as high as 50 ng m⁻³ after the bushfire period based on a pinic acid response factor to ESI/TOFMS. This study demonstrates the importance and influence of local vegetation patterns to the BVOC emissions and SOA precursors.

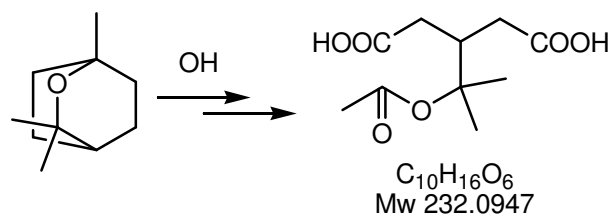


Figure 1. A proposed structure of a cineole oxidation product (C₁₀H₁₆O₆).

PREDICTION OF PARTICLE DISPERSION IN ATMOSPHERIC BOUNDARY LAYER USING LARGE-EDDY SIMULATION

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The atmospheric boundary layer (ABL) is the lower part of the atmosphere, in which turbulence plays an essential role on the transport of momentum and scalars (heat, water vapor and chemicals) between the biosphere and upper atmosphere. In the atmospheric boundary layer, the scales associated with turbulent motions range from the Kolmogorov dissipation scale (on the order of millimeter) to the boundary layer depth (on the order of a kilometer). The largest eddies are responsible for the turbulent transport of the scalars and momentum whereas the smallest ones are mainly dissipative.

Quantifying the transport rate and dispersion of chemicals from the Earth's surface into the upper parts of the atmosphere is of critical importance for a wide range of environmental applications, including pollutant dispersion in the atmosphere, contaminant transport in industrial applications, and transport of pollutants in the atmosphere. An open question regarding the prediction of particle-laden turbulent flows is how to represent the effects of boundary layer physical process, in particular turbulence, on the transport of chemical compounds.

The use of large-eddy simulation (LES) in the study of atmospheric boundary layer is being increasingly employed to describe turbulence dominated processes. LES consists of explicitly resolving all scales larger than the grid scale (on the order of meters in the ABL), while the smallest (less energetic) scales are parametrized using a subgrid-scale (SGS) model.

We present an efficient particle dispersion Eulerian-Lagrangian algorithm for the prediction of (carbonaceous) particle dispersion in the atmospheric boundary layer (ABL). The continuous phase is determined by large-eddy simulation (LES) in an Eulerian framework whereas the dispersed phase is simulated in a Lagrangian framework. The Lagrangian particle tracking requires that the instantaneous velocity of the flow to be known at the particle location. Accurate prediction of instantaneous velocity is of critical importance when the Lagrangian particle tracking is employed. Due to the wide range of length and time scales present in turbulent flows, large-eddy simulation is a suitable approach for high Reynolds flows providing an accurate prediction of the instantaneous flow field.

Preliminary results show that the Lagrangian particle tracking using LES can accurately predict the trajectory of particle as well the particle dispersion.

ANALYZING BIOMASS BURNING PARTICLE COMPOSITION WITH INFRARED SPECTROSCOPY

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Biomass burning is a significant contributor to the particulate organic carbon in the atmosphere, and understanding the composition and chemical fate of these particles is necessary for predicting their effects on atmospheric chemistry, air quality, and climate. As climate change influences the frequency and severity of boreal forest fires, the influence of biomass burning aerosols on the atmosphere may become significantly greater. Only a small portion of the organic carbon (OC) fraction of these particles has been identified at the molecular level, although several studies have explored the general chemical classes found in biomass burning smoke. To complement those studies and provide additional information about the reactive functional groups present, we are developing a method for polarity-based separation of compound classes found in the OC fraction, followed by infrared spectroscopic analysis of each polarity fraction. It is our goal to find a simple, relatively low-tech method which will provide a moderate chemical understanding of the entire suite of compounds present in the OC fraction of biomass burning particles. Method development and preliminary results will be presented.

THE DIFERENTIAL GLOBAL AND REGIONAL CLIMATE AND AIR-POLLUTION-HEALTH EFFECTS OF FOSSIL-FUEL VERSUS BIOFUEL SOOT

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The composition of biofuel soot differs significantly from that of fossil-fuel soot, yet the comparative effects on global and regional climate and air pollution health of these two types of soot have not been investigated. Here, global simulations with the GATOR-GCMOM model were performed to examine the effects. The model considered the evolution of soot emissions from externally- to internally-mixed by treating two discrete size distributions - an emitted-soot and an internally-mixed distribution. Emitted soot could become internally-mixed by coagulation and condensation. Emitted fossil-fuel soot consisted primarily of organic carbon, black carbon, and some sulfate. Biofuel soot consisted of a larger ratio of organic carbon to black carbon and several more inorganic chemicals than fossil-fuel soot. Both types of soot could take up water and obtain coatings. Size-resolved clouds and precipitation formed on both internally- and externally-mixed aerosol distributions, and aerosol inclusions were tracked in all cloud and precipitation particles. Results indicate that, in the global average, most heating from anthropogenic black carbon was due to heating from fossil-fuel soot, as biofuel-soot particles tended to take on more water and enhance cloudiness more readily than fossil-fuel soot particles, as expected. Because the heating due to fossil fuel soot was so strong, controlling it should reduce global warming substantially and more than controlling biofuel soot. However, control of biofuel soot was found to reduce more ozone- and particulate matter-related mortality particularly since biofuels are generally emitted in highly-populated regions of the world.

PARTICULATE CARBONYLS FROM GASOLINE AND DIESEL MOTOR VEHICLES

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Carbonyl emissions from gasoline powered light-duty vehicles (LDVs) and heavy-duty diesel powered vehicles (HDDVs) operated on chassis dynamometers were measured using an annular denuder-quartz filter-polyurethane foam sampler. Chemical analysis was performed with *O*-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine (PFBHA) derivatization in conjunction with chromatography-mass spectrometry. Two internal standards were utilized for quantification based on carbonyl recovery experiments, 4-fluorobenzaldehyde for $<C_8$ carbonyls and 6-fluoro-4-chromanone for $\geq C_8$ compounds. Gas- and particle-phase emissions for 39 aliphatic and 20 aromatic carbonyls ranged from 0.1 – 2000 $\mu\text{g/L}$ fuel for LDVs and 1.8 – 27000 $\mu\text{g/L}$ fuel for HDDVs. Gas-phase carbonyls accounted for 81-95% of the total carbonyls measured from LDVs and 86-88% from HDDVs. Particulate carbonyls emitted from a HDDV under realistic driving conditions were similar to concentrations measured in the NIST 1650 diesel particulate matter (PM) standard reference material. Carbonyls accounted for 19% of particulate organic carbon (POC) emissions from low-emission LDVs and 37% of POC emissions from three-way catalyst equipped LDVs. This finding identifies carbonyls as one of the largest classes of compounds in LDV PM emissions. The carbonyl fraction of HDDV POC was lower, 3.3-3.9% depending upon the operational conditions. The greater abundance of carbonyls associated with LDV particulate emissions versus emissions from HDDVs is consistent with previous measurements of higher volatility particles near freeways having minimal HDDV influence. Partitioning analysis indicates the carbonyls had not achieved equilibrium between the gas- and particle-phase under the dilution factors of 126-584 used in the current study. Further research is needed to measure the phase partitioning of carbonyl emissions at greater levels of sample dilution in order to enhance understanding of the ultimate environmental fate of the emissions.

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COMPARISON OF AEROSOL LIGHT ABSORPTION COEFFICIENT MEASUREMENTS AT THE MACE HEAD ATMOSPHERIC RESEARCH STATION USING A MAAP AND AN AETHALOMETER

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Continuous measurements of aerosol absorption coefficient are made at the Mace Head Atmospheric Research Station, near Carna, Co. Galway on the west coast of Ireland. A MultiAngle Absorption Photometer (MAAP) is used to measure aerosol absorption coefficient at the site as well as an Aethalometer (Model AE-16) at a 5-minute frequency. Analysis is presented here for the 2007 data set, using hourly values of aerosol absorption coefficient.

In the case of clean marine conditions, using a clean wind sector of 190 – 300 degrees, combined with a low value of absorption coefficient of $< \sim 1.0 \text{ Mm}^{-1}$, poor correlation ($R^2 = 0.025$) is found between the data from the MAAP and the Aethalometer. However in the case of polluted conditions (for a wind sector between 45 – 145 degrees combined with values of absorption coefficient $> \sim 1.0 \text{ Mm}^{-1}$) significant correlation ($R^2 = 0.89$) is found between the 2 instruments. The Aethalometer registers higher absorption coefficients (by a factor of $\sim 1.6 - 1.65$) than the MAAP, for absorption coefficients $> \sim 1.0 \text{ Mm}^{-1}$. Under these conditions, use of quoted absorption cross sections of the MAAP ($\sigma_{\text{BC}} = 6.6 \text{ m}^2 \text{ g}^{-1}$) and of the Aethalometer ($\sigma_{\text{Aeth}} = 16.6 \text{ m}^2 \text{ g}^{-1}$) entails that inferred black carbon mass concentration is a factor of $\sim 50\%$ higher as determined from the MAAP, compared to the Aethalometer.

COMPARISON OF SUGAR COMPOSITION IN FINE PARTICULATE MATTER AT FOUR SITES IN EASTERN TEXAS AND CENTRAL ARIZONA

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Abstract:

Sugars in aerosols have been proposed in many studies as a primary marker for biogenic carbon associated with biomass burning and atmospheric entrainment of soil. In an effort to quantify the contribution of wood smoke and agricultural soils to ambient particulate matter at different locations, a series of fine PM samples were collected at two rural sites (San Augustine) and one urban site (Dallas) in Texas from November 2005 to July 2006. Following that, another series of fine and coarse PM samples were collected from January to April 2008 near Higley, AZ, a location of rapid urbanization in a traditionally agricultural location. In these two studies, various sugar compounds including monosaccharides, anhydrous sugars, disaccharides and saccharide polyols were quantified in both fine and coarse PM samples, and carbohydrate markers specific to soil organic matter were used along with other particulate matter tracers in a Positive Matrix Factorization (PMF) model to separate entrainment of agricultural soils from other fugitive dust sources. Local soil samples taken at selected sites were also analyzed to determine soil sugar compositions for comparison with ambient aerosol sugars. A comparison between urban and rural locations was used to evaluate seasonal variation and the impact of different sources at each of the four sampling locations. The difference of contribution from agricultural sources to ambient fine PM was also compared between the high humidity sites in Texas sites and more arid location in Arizona.

Keywords: sugars, ambient particulate matter, molecular markers, Texas, Arizona

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INFLUENCE OF TEMPERATURE AND WATER ON SECONDARY ORGANIC AEROSOL FORMATION FROM THE OZONOLYSIS OF LIMONENE, Δ^3 -CARENE AND α -PINENE

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Abstract

Vegetation emits large number of biogenic volatile organic compounds (BVOC). In the atmosphere these compounds are oxidised primarily by ozone, OH radicals and NO_3 radicals and the relative importance depends on chemical structure of the organic compound and concentrations. In the degradation process compounds with low volatility can be formed which may undergo gas-to-particle conversion, hence contributing to the formation of secondary organic aerosol (SOA). One important group of compounds contributing to SOA formation is the monoterpenes ($\text{C}_{10}\text{H}_{16}$), where globally α -pinene and limonene are the most abundant. In this work the impact of temperature, relative humidity (RH) and radical chemistry on the aerosol formation from ozonolysis of limonene, Δ^3 -carene and α -pinene have been investigated. In the ozonolysis OH radicals are formed which can react with the precursor terpene or products if not accounted for by the addition of an OH scavenger.

The experiments were conducted by using the G-FROST (Göteborg-Flow Reactor for Oxidation Studies at low Temperatures) set-up. This set-up consists mainly of a laminar flow reactor (length: 1.9 m and i.d.:10 cm) and a scanning mobility particle sizer (SMPS) system where particle number and mass size distributions were obtained. This is a set-up where temperature, relative humidity and concentrations can be carefully controlled. The flow reactor and the SMPS-system are housed in a temperature controlled chamber, where the temperature can be varied between 243 and well above 323 K. Data will be presented for the reaction temperatures 243, 273 and 298 K and for relative humidities between dry and 80 % and when using 2-butanol or cyclohexane as OH scavengers as well as without any scavenger in the system. Below are examples illustrating the effect of water and scavenger on SOA formation (Fig.1 & 2). Another important result is the evidence of OH radical production from the ozonolysis at low temperatures. The results are discussed in relation to the current knowledge of the degradation mechanism.

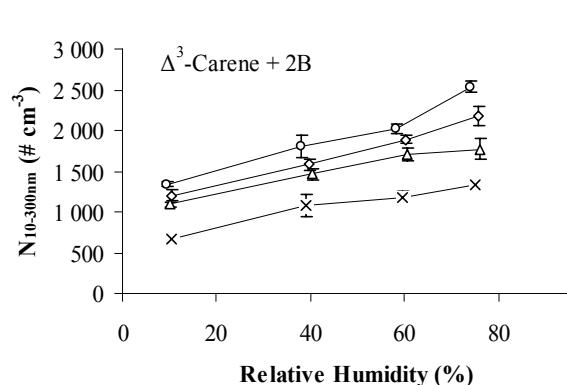


Fig. 1. Effect of OH scavenger concentration on the number of particles formed in the ozonolysis of Δ^3 -carene. The concentration is increasing in the order circles, diamonds, triangles and crosses ($3.5\text{--}32 \times 10^{13}$ molecules cm^{-3}).

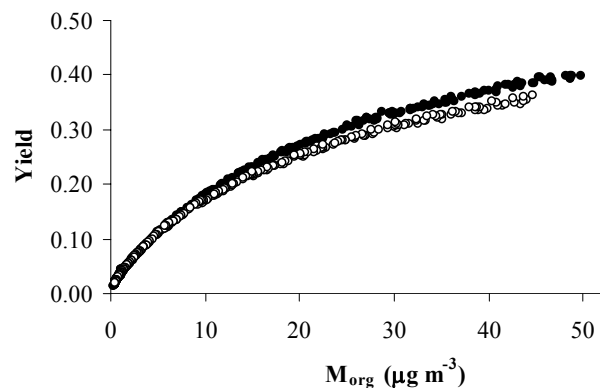


Fig. 2 The yield of SOA from limonene ozonolysis with 2-butanol (2B) as scavenger. Black circles RH 60% and white circles dry conditions, 298 K.

Particle and gas phase analysis of carbonyl compounds formed during monoterpene oxidation in chamber experiments

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Particulate matter in the atmosphere has many sources including direct emission from combustion and industrial processes as well indirect formation, like the oxidation of monoterpenes.

The atmospheric degradation of monoterpenes produces multifunctional compounds with different properties (e.g. vapour pressure, polarity) so that the products can contribute to the gas phase as well to the particle phase. The first generation oxidation products of monoterpenes are mainly carbonyl compounds with semi volatile characteristics. They are commonly found in both ambient and chamber experiment samples. To determine the yields of carbonyl compounds from monoterpenes and their first generation oxidation products, an analytical method with 2,4-dinitrophenylhydrazine (DNPH) was adapted (Grosjean and Grosjean, 1995). The acid-catalysed derivatisation with DNPH leads to stable 2,4-dinitrophenylhydrazones, which can be characterised with HPLC and MS detection. The use of DNPH derivatisation and HPLC/ESI-TOFMS (Electrospray Ionisation Time-Of-Flight Mass Spectrometry) offers several advantages because of its high sensitivity and the determination of the exact chemical formula for the identification of unknown carbonyl compounds. Aerosol chamber experiments were carried out in the "Leipziger Aerosol Kammer" (LEAK) which is made of Teflon[®] foil and has a volume of 19 m³. Under the controlled conditions aerosol studies are performed to improve the knowledge of the chemical composition of organic aerosols. The secondary organic aerosol (SOA) formation from the ozonolysis of α -pinene and β -pinene was studied in the presence of different seed particles. The ozonolysis experiments were carried out with ammonium bisulfate or acidic ammoniumsulfate seed particles. The resulting compounds were sampled by a denuder/PTFE filter combination for the determination of the gas- and particle-phase products. In this study results were shown from the carbonyl-analysis of the filter samples. Therefore the PTFE filters were extracted and afterwards derivatised with DNPH, following by the HPLC/ESI-TOFMS analysis. Pinonaldehyde from the α -pinene ozonolysis and nopinon from the ozonolysis of β -pinene were quantified via the synthesised standard compounds. The results are compared with the product yields from the gas-phase as well with other analytical techniques from the literature (Yu et al., 1999).

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CARBONACEOUS PARTICLE CONCENTRATIONS SINCE THE PRE-INDUSTRIAL ERA FROM ASIAN ICE CORES

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Due to the existence of only a few historical records of carbonaceous particles (CP), studies assessing the role of CP in climate change have relied on estimated inventories of CP concentrations based on wood and/or fossil fuel consumption data. However, many important CP sources such as residential emissions from cooking and heating are very difficult to estimate in the present, even more difficult to estimate for the past, and can vary greatly through time and with location. Thus, more quantitative measurements of CP emissions and atmospheric concentrations as a function of time are needed to estimate climate change related to CP forcing.

We use ice core records from the Tibetan Plateau (Mt. Nyainqentanglha and Mt. Geladandong) to produce records of CP concentrations spanning pre-industrial to modern time. Ice cores from mountain glaciers provide high-resolution archives of past atmospheric and environmental conditions, and preserve information about natural and anthropogenic atmospheric composition, and aerosol and contaminant transport and deposition. CP deposition histories from this region are key to understanding the climatic impacts of CP, as the atmospheric composition in this region is influenced by the largest sources of CP globally.

We analyzed the ice cores by combining optical (wavelength dependent in the near-ultraviolet to near-infrared spectral region) and thermal methods to determine concentrations and sources of black carbon, elemental carbon and organic carbon through time. Additionally, the optical and chemical properties of mineral dust in the ice core were investigated. Preliminary results will be presented.

BLACK CARBON IN SOUTH ASIAN MEGACITIES

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Air pollution in South Asian cities has grown with progressive industrialization and urbanization. The region is one of the most densely populated in the world, with present population densities of 100-500 persons km⁻². There are 6 megacities with population around or above 10 million in the region: Kolkata, Mumbai, Delhi, Dhaka, Lahore and Karachi. The level of air pollution in Pakistan's two largest cities, Karachi and Lahore, is estimated to be 20 times higher than World Health Organization standards, and it continue to rise. The number of motor vehicles in Pakistan has doubled in recent years from 2.7 million in 1990 to 5.4 million in 2005. With few controls on vehicular emissions and little enforcement, reports show that motor vehicle exhaust accounts for 90 per cent of the pollutants in Pakistan. Therefore, we measured the concentrations of black carbon [BC] at Lahore, Pakistan from November 22, 2005 to January 31, 2006 with an Aethalometer every 5 min. [BC] were very high, ranging from about 5 to 110 $\mu\text{g m}^{-3}$, with a mean of 21.7 $\mu\text{g m}^{-3}$, with a mean of 21.7 $\mu\text{g m}^{-3}$. A distinct diurnal variation was observed: concentrations were lowest from about 10 a.m. to 4 p.m. local time, and highest around 5 to 9 p.m. No clear relationship was observed between surface wind directions and BC, although some of the highest concentrations were observed when the air flow was from southwest to northwest. The daily variations in the concentrations were strongly affected by the diurnal variations in the mixing height; BC concentration were low during the day when the mixing heights were high, ~1000 meters, and very high at night when the mixing heights were low <250 meters. Periods of light to dense fog occurred from 22 December through 4 January. [BC] were generally lower than average when fog occurred during the night and early morning, but they were not necessary lower during daytime fogs. We also collected aerosols on quartz filters every 3, 6, or 12 h and determined the concentrations of elemental, [EC], and organic carbon, [OC], using the thermal-optical method. The [BC] were highly correlated with EC ($r^2 = 0.71$), but on average 25% higher than [EC]. The [EC] and [OC] concentration were moderately correlated ($r^2 = 0.65$). The [OC]/[EC] ratios varied from 2.8 to 12, with a mean of 5.6. Although a large component of the carbonaceous aerosols in Lahore originated from fossil fuel combustion, a significant fraction was derived from biomass burning. Nearly two-thirds of the fine particle, PM_{2.5}, mass was contributed by the carbonaceous aerosols.

MEASUREMENT OF AEROSOL REFRACTIVE INDEX BY POLAR NEPHELOMETER

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Using the polar nephelometer measurements, we seek to determine the refractive indices for carbonaceous aerosols. The refractive indices are a basic optical property of aerosol particles to determine the parameters relevant to the single scattering albedo, asymmetry factor and specific absorption. The polar nephelometer measures the scattered light intensities into 21 discrete scattering angles where a stream of aerosol particles intersect a laser beam. Incident light is provided by a 350 milliwatt diode laser beam with a wavelength of 670 nm and its plane of polarization is periodically changed from parallel to the scattering plane to perpendicular to it by a computer controlled electromechanically operated a half wave plate. This scattering information is combined with simultaneously measured size distribution information, and is used to determine the real refractive index of the aerosols using a genetic algorithm search method. The genetic algorithm method is very effective because this is not an analytical solution, therefore not limited to Mie Scattering.

Model aerosols including polystyrene latex spheres, ammonium sulfate aerosol and nigrosin particles are used to verify the technique theoretically and experimentally. The real refractive index of polystyrene latex spheres and ammonium nitrate particles are determined and match expectations within experimental uncertainties using Mie-Lorenz theory. Work on Nigrosin is on-going. Refractive index determination for spherical aerosols generated by oxidizing α -pinene indicate that they are not homogeneous.

Characteristics of carbonaceous aerosol in Guangzhou during the 2006 PRD campaign: optical properties and mixing state

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Abstract

In order to characterize the causes of air quality degradation in the metropolitan area of Guangzhou, China, aerosol optical and chemical measurements were conducted from 2 to 31 July 2006 at a Guangzhou urban site as part of the Observation Experiment for Regional Air Quality in Pearl River Delta (PRD) of China. Light absorption coefficient and carbonaceous aerosol components (OC and EC) were measured by an aethalometer and a Sunset elemental carbon/organic carbon (EC/OC) field analyzer, respectively. Atmospheric conditions were categorized into three types; local haze (LH), long-range transport haze (LRT), and clean marine (CM) based on the meteorological conditions and aerosol potassium ion (K^+) concentration. Average OC during CM, LH1, LH2, LRT1, and LRT2 periods was determined to be 5.4 ± 2.9 , 15.9 ± 5.9 , 12.0 ± 7.9 , 13.9 ± 5.3 , and $16.9 \pm 6.4 \mu\text{g m}^{-3}$, respectively while average EC was 3.9 ± 1.9 , 6.8 ± 2.5 , 5.8 ± 3.0 , 5.4 ± 1.7 , and $6.5 \pm 2.5 \mu\text{g m}^{-3}$, respectively. Average OC/EC ratio during Marine, LH1, LH2, LRT1, and LRT2 periods was determined to be 1.5 ± 0.6 , 2.4 ± 0.6 , 1.9 ± 0.8 , 2.8 ± 1.2 , and 2.8 ± 1.0 , respectively. Average minimum OC/EC ratio was obtained to be 1.06 ± 0.28 under low photochemical processing condition (6~8 A.M.). Average fraction of secondary OC to total OC was determined to be $41.6 \pm 23.8 \%$ with a minimum of $26.8 \pm 16.8 \%$ in the morning (7 A.M.) and a maximum of $64.4 \pm 8.7 \%$ at noon. Secondary OC was determined based on the minimum OC/EC ratio method. It was found that secondary OC formation was highly correlated with ambient temperature as the secondary OC formation rate of $1.5 \mu\text{g C m}^{-3}/\text{C}^\circ$ under ambient temperature $> 31^\circ\text{C}$. Average shadowing effect was determined to be $12.3 \pm 4.7 \%$ of total light attenuation, resulting in $12.3 \pm 4.7 \%$ underestimation of EC by aethalometer. Diurnal variation of light attenuation coefficient (b_{ATN})/EC ratio was similar to that of secondary OC with a low in the morning and a high in the afternoon, which suggests the enhancement of light attenuation in the morning by the internal mixing of EC with secondary aerosols such as secondary OC and sulfate. Minimum b_{ATN} /EC ratio method was used in this study to determine the additional absorption by the internal mixing of EC. It was found that 19.4 % of total b_{ATN} was due to additional absorption by the internal mixing of EC. Generally high contribution of the additional absorption by the internal mixing of EC to total b_{ATN} was observed during the LH and LRT periods.

GOT MILK? MAKING AND MEASURING COLLOIDAL SUSPENSIONS OF BLACK CARBON IN WATER

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Suspensions of black carbon (BC) in water can be useful in laboratory experiments, including the generation of internally mixed BC-containing aerosols, BC-contaminated snow, and a stable aerosol supply for comparing various BC or light-absorption measurement methods. However, BC is generally hydrophobic and does not mix with water.

We developed a method of preparing a BC hydrocolloid, wherein the BC particles are dispersed evenly throughout water, yielding the appearance of a gray to black solution, depending on the amount of BC suspended. We collect BC generated with a diffusion flame of methane and air onto stretched Teflon membrane filters. The BC is initially hydrophobic and does not mix with water, rather it clusters at a water surface. Exposure to ozone transforms the BC from a hydrophobic to a hydrophilic state. After ozonation, the BC is readily removed from the filter by rinsing it with water. A simple swishing of the rinse water in a beaker is sufficient to form the hydrocolloid. We find that ozonation is highly effective in yielding the desired (electrostatic) stabilization, which prevents the BC particles from aggregating and settling. The BC suspensions are stable for several months if not longer.

We find that only the BC generated with our diffusion flame – which we previously noted does not contain an appreciable amount of organic carbon – can be turned into a hydrocolloid. Other BC-containing particles, such as from diesel exhaust or burning biomass, remain largely hydrophobic after ozonation. Also noteworthy, we find that passing the diffusion flame-generated BC through black conductive silicon tubing (from TSI) precludes the transformation from hydrophobic to hydrophilic. (Since this type of tubing is widely used in aerosol research, further exploration and caution when using it in studies of aerosol hygroscopic properties is warranted.)

We use a custom spectrometer equipped with a liquid waveguide capillary cell to quantify the amount of BC in suspension. This capillary cell increases measurement sensitivity by 100-fold compared to a conventional cuvette cell. Suspensions with increasing amounts of BC were prepared to develop a calibration curve for this technique. Absorbance is linear with BC content and the limit of detection is approximately 5ppb.

JOINT EFFECT OF ORGANIC AND INORGANIC AEROSOL COMPONENTS ON CLOUD DROPLET ACTIVATION

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The effect of organic aerosol constituents on cloud droplet activation (and thereby on indirect aerosol forcing) received particular attention in the past few years. Köhler theory is often used to calculate the critical supersaturation corresponding to an aerosol particle of known dry size and composition. The reliability of such calculations strongly depends on the input parameters of the model, namely the surface tension and the water activity of the solution formed on the aerosol particle. These properties are known for the solutions of the major inorganic aerosol constituents but hardly any information is available on the organic fraction of atmospheric aerosol.

In this study surface tension and water activity were determined at different concentration levels for nine organic acids. The surface tension depression was influenced by the size of the hydrophobic part and the number of polar functional groups in the molecule while water activity was primarily determined by the dissociation constant of the acid. Mixtures of organic acids and inorganic salts (NaCl and (NH₄)₂SO₄) were also investigated. It was found that inorganic salts may enhance the surface tension depression of organic compounds. Humic-like substances (HULIS) isolated from ambient aerosol were found to lower surface tension more than aquatic and terrestrial fulvic/humic acids or any relevant organic acid ever studied. As far as the combined effect of inorganic and organic constituents is concerned, it was found that the critical supersaturation of rural aerosol particles was very similar to that of pure ammonium-sulfate while the mass of potential CCN was considerably increased by the presence of organic compounds.

Humic-Like Substances in Airborne Particulate Matter: Seasonal Trends and Possible Sources

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The presence of Humic-like substances (HULIS), also referred to as organic macromolecules and polyacids, in airborne particulate matter was reported as early as 1980 (Simoneit et al., 1980). Since then, numerous studies have been conducted to shed light on chemical structure, physical properties and formation pathways of these macromolecular compounds that contribute to atmospheric organic carbon with up to 50 %. Figure 1 visualises the increasing interest since the term HULIS was coined by Havers et al. in 1998.

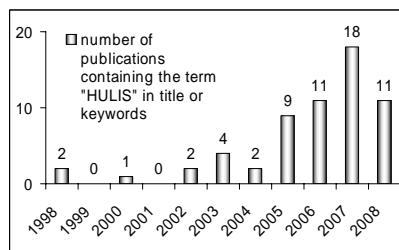


Figure 1: Histogram of publications

Atmospheric HULIS levels have been quantified by using a two step separation technique with subsequent carbon-specific detection (Limbeck et al., 2005) and contributions of HULIS to organic carbon between 6 and 40 % have been revealed for background sites in a European west east transect and for intra urban and remote sites, respectively (Feczko et al., 2008; Wonaschütz et al.,

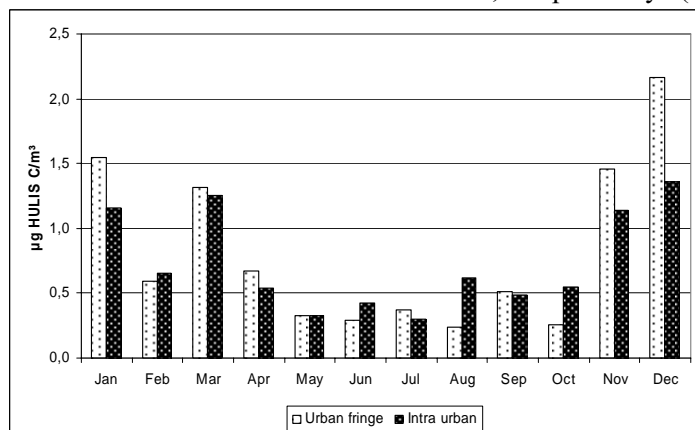


Figure 2: Monthly averaged HULIS C concentration (n=2-14)

depicted in figure 2. Lowest concentration levels were found during summer season with 0.2 µg HULIS C/m³. The highest monthly mean occurred in December at the urban fringe site with 2.2 µg C/m³. Seasonal averaged winter enrichment factors of 2 and 4, have been found for the intra urban and the urban fringe site, respectively. Monthly HULIS averages strongly correlated with levels of the biomass combustion tracer levoglucosan for both sites ($R^2 \sim 0.8$) what indicates biomass combustion products to be a source for HULIS formation.

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CONTRIBUTION OF RESIDENTIAL WOOD COMBUSTION TO HOURLY WINTER AEROSOL IN NORTHERN SWEDEN DETERMINED BY POSITIVE MATRIX FACTORIZATION

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The combined effect of residential wood combustion (RWC) emissions with stable atmospheric conditions, which is a frequent occurrence in Northern Sweden during wintertime, can deteriorate the air quality even in small towns. To estimate the contribution of RWC to the total atmospheric aerosol loading, the positive matrix factorization (PMF) method was applied to hourly mean particle number size distributions measured in a residential area in Lycksele during winter 2005/2006. The sources were identified based on the particle number size distribution profiles of the PMF factors, the diurnal contributions patterns estimated by PMF for both weekends and weekdays, and correlation of the modeled particle number concentration per factor with measured aerosol mass concentrations (PM_{10} , PM_1 , and light-absorbing carbon M_{LAC}). Through these analyses, the factors were identified as local traffic (factor 1), local RWC (factor 2), and local RWC plus long-range transport (LRT) of aerosols (factor 3). In some occasions, it was difficult to detach the contributions of local RWC from background concentrations since their particle number size distributions partially overlapped and the model was not able to separate these two sources. As a consequence, we report the contribution of RWC as a range of values, being the minimum determined by factor 2 and the possible maximum as the contributions of both factors 2 and 3. A multiple linear regression (MLR) of observed PM_{10} , PM_1 , total particle number, and M_{LAC} concentrations is carried out to determine the source contribution to these aerosol variables. The results reveal RWC is an important source of atmospheric particles in the size range 25-606 nm (44-57%), PM_{10} (36-82%), PM_1 (31-83%), and M_{LAC} (40-76%) mass concentrations in the winter season. The contribution from RWC is especially large on weekends between 18:00 LT and midnight whereas local traffic emissions show similar contributions every day.

EXTRACTABLE CARBONACEOUS PARTICULATE MATTER AND GC/MS CHARACTERIZATION OF POLAR FRACTION

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Carbonaceous species are recognized contributors to radiative forcing. While the contribution of black or elemental carbon has been discussed, only a few studies have attempted to address the impact of organic carbon (OC). The characterization of the OC fraction is particularly difficult because it may represent thousands of species with different physical-chemical properties. Consequently, typical analytical approaches do not represent OC in comprehensive manner. They either 1) determine a total OC employing thermal optical transmittance/reflectance (TOT/TOR) methods, or 2) characterize a limited portion of OC (20–60%) on a molecular level by gas chromatographic/mass spectrometric analysis (GC/MS). Besides the fact that those two measurements are rarely reported at the same time, it is unclear whether limitation in the detailed characterization is due to the extractability and/or elutability from GC/MS.

Thus the aim of the presented study was to evaluate a potential of two extraction/fractionation methods from three particulate matter (PM) samples (e.g., wood smoke, diesel exhaust SRM 2975 and urban PM SRM 1648). Both extraction methods using hot pressurized water (25–250 °C) and a series of organic solvents (hexane, methylene chloride, methanol) on Soxhlet achieved similar recoveries of ~50% and ~70% of extractable OC based on TOT and TOR, respectively. Both extraction methods also provided similar distribution of OC in different polarity fractions. The distribution of organics in wood smoke PM extracts reflected the polar nature of wood smoke PM. For diesel exhaust PM (which is considered non-polar due to a high content of EC), a significant portion of organics was found in the polar fractions using both extraction methods. This corroborates the results of toxicological studies showing a significant toxicity for the methanol fraction of diesel exhaust OC.

Further characterization of obtained fractions (prior and after trimethylsilylation) was performed using GC/MS. The GC/MS analysis revealed that composition of the obtained extracts is not only affected by the polarity of the solvent, but also by the matrix-analyte interactions. For example, dicarboxylic acids were found in different polarity fractions obtained from wood smoke, diesel exhaust PM, and urban PM representing primary, and combination of primary and secondary emissions, respectively. While majority of dicarboxylic acids in urban PM was extracted in water-soluble fraction, the same acids were recovered more efficiently with higher temperature water (less polar) from wood smoke and diesel exhaust PM. This may be due to stronger embedding of dicarboxylic acids into the matrix in primary emission PMs (i.e., wood smoke, diesel exhaust PM) than when formed during secondary atmospheric processes (i.e., urban PM). This finding was observed also for other species and suggests that fractionation of organic PM based on the polarity of extracting solvent depends on the analyte-matrix interactions, which may be useful when accounting for the availability of those analytes in atmospheric processes.

STABLE CARBON AND NITROGEN ISOTOPIC COMPOSITION OF BIOMASS BURNING AEROSOLS AND THEIR MOLECULAR COMPOSITION OF DIACIDS AND RELATED COMPOUNDS: LBA-SMOCC CAMPAIGN FROM RONDÔNIA, BRAZIL

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Abstract: As part of the Large-Scale Biosphere-Atmosphere Experiment in Amazonia–Smoke, Aerosols, Clouds, Rainfall and Climate (LBA-SMOCC) campaign, PM_{2.5} aerosols (n=11) were collected at Rondônia, Brazil, during intensive biomass burning episodes on 16-25 September 2002 using a high volume dichotomous virtual impactor equipped with front/back-up system of quartz fiber filter. We determined concentrations of total carbon (TC) and nitrogen (TN) in aerosols and their stable carbon ($\delta^{13}\text{C}$) and nitrogen ($\delta^{15}\text{N}$) isotopic ratios using EA and EA-IRMS. TC contents were 34-86 μgm^{-3} (av. 60 μgm^{-3}) whereas TN contents were 0.51-3.44 μgm^{-3} (av. 1.83 μgm^{-3}). The averaged TC/TN ratio was found to be 40 ± 21 (range: 20-84), being higher than urban aerosols (e.g., ca. 2-16 in Tokyo aerosols). The $\delta^{13}\text{C}$ ranged from -25.03 to -23.54‰ (av. $-24.27 \pm 0.54\text{‰}$). Using a two end member model (C_3 plants: -30.5‰ and C_4 plants: -13.5‰), contribution of C_3 plants to TC was calculated to be $68 \pm 3.2\%$ and that of C_4 plants to be $32 \pm 3.2\%$. This study demonstrates that major source of biomass burning aerosols in Amazon is C_3 plants. The $\delta^{13}\text{C}$ of water-insoluble organic carbon (WISOC) ranged from -26.27 to -25.62 (av. $-24.83 \pm 0.53\text{‰}$). Based on mass balance equation for TC and WISOC, $\delta^{13}\text{C}$ of water-soluble organic carbon (WSOC=TC-WISOC) was estimated to be $-23.33 \pm 0.73\text{‰}$, indicating a slight enrichment of ^{13}C in WSOC. The contribution of WSOC to TC was found to be 55-71%, indicating a water-soluble nature of organic aerosols produced by biomass burning processes. The $\delta^{15}\text{N}$ of TN and water-insoluble organic nitrogen (WISON) were determined to be 18.8‰ to 23.2‰ (av. $21.7 \pm 1.29\text{‰}$) and 8.5‰ to 15.3‰ (av. $11.8 \pm 2.2\text{‰}$), respectively. We estimated $\delta^{15}\text{N}$ of water-soluble organic nitrogen (WSON=TN-WISON) in the aerosols to be $22.73 \pm 1.55\text{‰}$, using a mass balance equation for TN and WISON.

Homologous series dicarboxylic acids ($\text{C}_2\text{-C}_{11}$) and related compounds (ω -oxocarboxylic acids, pyruvic acid and α -dicarbonyls) were identified, for the first time, in the Amazonia biomass burning aerosols, using a capillary GC and GC/MS. Among all the species, oxalic acid was found to be the most abundant species followed by succinic, malonic and glyoxylic acid. Averaged concentrations of total diacids, oxoacids and dicarbonyls were found to be $2561 \pm 501 \text{ ngm}^{-3}$, $157 \pm 42 \text{ ngm}^{-3}$ and $94 \pm 22 \text{ ngm}^{-3}$, respectively. They are several times higher than those reported in urban aerosols such as 14 Chinese megacities. Relative abundances of individual diacids in total diacids stayed almost constant during the campaign; e.g., oxalic: $58 \pm 0.48\%$, succinic: $11 \pm 0.39\%$ in daytime and oxalic: $60 \pm 1.95\%$, succinic: $13 \pm 0.13\%$ in nighttime. Contributions of total diacids to TC were calculated to be $1.6 \pm 0.46\%$ in daytime and $1.4 \pm 0.32\%$ in nighttime. These values are slightly higher than those (0.95%) reported in urban aerosols from Tokyo, but lower than those (8.8%) of the remote marine aerosols from the Pacific including tropics. Their contributions to WSOC were $2.4 \pm 0.41\%$ in daytime and $2.3 \pm 0.40\%$ in nighttime. The contribution of diacids plus related compounds to WSOC ranged from 2.1-3.5%. No significant changes were found for the concentrations of diacids and their relative abundances to total diacids, TC and WSOC. Temporal variations of diacids showed a similar trend with K and EC (biomass combustion tracers), indicating that major portions of diacids and/or their precursors are directly emitted from biomass burning.

PARTICULATE EMISSIONS BY A SMALL NON-ROAD DIESEL ENGINE: (I) BIODIESEL AND DIESEL CHARACTERIZATION AND (II) EFFECT OF METAL SALTS AND SULFATES ON EGA MEASUREMENTS

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Particulate emissions from a 4.8 kW diesel generator running on ultra-low sulfur diesel and biodiesel fuels are characterized as a function of engine load. Number distributions measured by a scanning mobility particle sizer (SMPS) show that particle mobility diameters rise with increasing engine loads. The elemental carbon (EC) to organic carbon (OC) ratio, measured by thermo-optical transmission evolved gas analysis, with careful attention to the potential for an OC artifact, increases from about 0.5 at idle load to 3.8 at 100% load when using diesel fuel. Transmission electron microscopy (TEM) images of the particles showed that at idle, the majority of the particles were liquid droplets the small remaining fraction were aggregates. When a load was applied, the droplets were replaced by chain aggregates, which had a mean primary particle size of 29 ± 9 nm at 100% load. Fractal dimensions averaged 1.63 ± 0.13 , consistent with much larger diesel engines emissions reported in the literature. The use of biofuel (B100) results in emissions of particles that are compact, irregular, and lack the clearly defined primary particles of diesel aggregates, and yet at max load they have similar EC/OC ratios as diesel particles.

Studies have suggested that inorganic constituents of the ambient aerosol can catalyze the oxidation of soot during evolved gas analysis (EGA). Mixtures of metal salts and diesel particulates on a quartz filter are analyzed and the evolution of carbon is compared to that of native diesel particles. In addition to mixing individual metal salts, the catalytic effect of metal salt combinations was also investigated. Preliminary results show that all metal salts investigated except for MgCl_2 and MgSO_4 , which had no effect, catalyzed the oxidation of soot. We observe that for almost all the experiments, the inclusion of metal salts to the soot aerosol resulted in reduced EC to total carbon (TC) ratios, although the degree of reduction was not necessarily correlated with the degree of change in oxidation temperature. The impact of metals on OC charring will also be discussed.

COMPARISON OF BLACK CARBON CONCENTRATIONS AMONG AT ROADSIDES, ON ROADS, AND IN ROADWAY TUNNELS

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Vehicles such as passenger cars and public buses are popular transportation. Diesel-fueled vehicles are known to emit smoke. Black carbon is a representative of diesel particles, and it plays a role in global warming due to the property of light absorption. In highly populated areas such as mega cities, many people are living near roads. Therefore, nearby traffic contamination is more important than urban air pollution monitored far away from roads. To catch exposure level of vehicle-related particulate matters in living environments, the mass concentration of black carbon was monitored using a portable aethalometer in roadway tunnels, on roads, and at roadsides in urban area of Seoul, Korea.

Intensive measurement of the black carbon concentrations for about one week at one fixed roadside site has been regularly monitored from once to four times per year by seasons since the year of 2005. In order to confirm the representative exposure level at the roadside in Seoul, additional measurements were carried out at four different roadsides once per each location. The black carbon concentrations were also monitored inside of passenger cars driving on real roads during 1~3 hrs in the early morning, morning rush hour, afternoon, and evening rush hour twice on September 2006 and January 2007. Roadway tunnel measurement can be used for obtaining reference exposure level of black carbon due to vehicles, and can minimize the effect of meteorological factors on black carbon concentration unlike roadside measurements. It was carried out inside of two roadway tunnels for two or four days per each measurement on April and September, 2005 and February 2007.

Average concentrations of black carbon measured on roads and at the roadsides are $21.5 \pm 8.4 \mu\text{g}/\text{m}^3$ and $6.6 \pm 1.8 \mu\text{g}/\text{m}^3$, respectively, which are 117% and 34%, respectively, to that measured in roadway tunnels. Averaged diurnal variation of black carbon concentrations at the roadsides and in roadway tunnels showed the minimum value in the early morning around 3~4 a.m., high concentration peak in the morning rush hour, and relatively small peak in the evening rush hour, which is similar to that of the traffic volume. The average black carbon concentrations exposed to a driver on roads were $10 \sim 12 \mu\text{g}/\text{m}^3$ in the early morning, $20 \sim 38 \mu\text{g}/\text{m}^3$ in the morning rush hour, and $18 \mu\text{g}/\text{m}^3$ showed in the evening rush hour, whose diurnal pattern is similar to that in tunnel and at roadsides. The highest black carbon concentrations among averaged diurnal variations at five different roadsides were found to be nearly the same of about $10 \mu\text{g}/\text{m}^3$ at 7~8 a.m. From these results, black carbon concentration data for the one fixed roadside monitoring site is concluded to stand for the representative exposure level of vehicle-related particulate matters in urban area of Seoul.

OPTICAL PROPERTIES OF MULTI-COMPONENT MIXTURES OF CARBONACEOUS DUSTS AND AEROSOLS

By

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Experiments were conducted to measure the optical properties of carbonaceous dusts (coal dust), non-carbonaceous dusts (limestone dust, (CaCO_3)), and combustion generated aerosols (of varying carbon content) as both single components and in multi-component mixtures. Parameters of interest for this study were the differential scattering cross sections, specific (or mass) extinction coefficients, single particle albedo, and refractive index. Of particular interest in this study were the changes in scattering and extinction that occur within multi-component mixtures and the development of realistic models to predict these effects.

For dusts, diesel exhaust particles, and their mixtures, experiments were performed in a large dust box (Marple chamber) where particles were injected at low rates near the top of the chamber and allowed to fall due to gravity to the bottom of the chamber where the measurements were made either *in situ* or by flowing the particles to external particle analysis instrumentation. For combustion generated aerosols, the particles were produced within one or more combustion chambers and then flowed into a smoke box where small fans were used to produce uniform concentrations. As with the dust box, particle measurements were made either *in situ* or by flowing the particles to external particle analysis instrumentation.

Aerosol mass concentrations were measured using either a Tapered Element Oscillating Microbalance (TEOM) or a TSI Dust Trak or, in some experiments, both. Measurements of light extinction were made at wavelengths of 546 nm, 635 nm, and 980 nm and multi-angle scattering measurements were made at wavelengths of 635 and 980 nm. In addition, for many of the experiments, simultaneous measurements were made using a calibrated ionization chamber and a condensation nuclei counter. Although not available for all of the experiments, an SMPS was used occasionally for measurement of the particle size distributions.

Results of the experiments generated single scattering albedos that varied directly with volatile mass fraction and inversely with the carbon mass fraction from a low value in the range of 0.17 to a maximum value near 0.50. Complex components of the index of refraction (extinction coefficients) showed a similar dependency. Optical extinction and scattering properties of dusts could be described adequately by the classical Mie theory while the smaller aerosols produced from combustion were better described by assuming fractal-like aggregates. Extinction, scattering, and hence absorption, from multi-component mixtures could best be predicted using mass-weighted averages of the individual components. This paper will discuss the experiments, the results obtained, and the implications of these results toward the refinement of radiative transfer models for dusts and aerosols.

BOUNDING ANALYSIS OF SECONDARY ORGANIC AEROSOL GROWTH IN THE VICINITY OF THE FOREST CANOPY

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Implementing the Regional Haze Rule in the West and other parts of the country requires that source apportionment of aerosols into natural (biogenic) and anthropogenic source categories be accomplished. Carbonaceous aerosols are large contributors to visibility degradation (extinction) in the West. The organic carbon (OC) content of atmospheric aerosol has been increasing for the in the inter-mountain west, and is an important component of aerosols. Secondary Organic Aerosol (SOA) of biogenic origin is a significant fraction of this OC aerosol, particularly in heavily forested or rural regions. We have been investigating SOA formation resulting from the oxidation of biogenic emissions in a forested ecosystem located in the Sierra Nevada Mountains in California. The site, established in 1997, provided a well-characterized field location and an established operational platform for observing atmospheric processes under actual atmospheric conditions. Measurements performed at the site include highly time-resolved measurements of meteorological variables, aerosol properties, the concentrations of aerosols, gas phase biogenic volatile organic hydrocarbons, and atmospheric oxidants within and out of a forest canopy. Data were collected during selected summer months of 2001, 2002, and 2003.

This presentation provides an analysis of the combined gas and particle-phase data to bound the amount of biogenic SOA formed in the immediate vicinity of the canopy. All of the aerosol formed during aerosol growth events observed at the site is assumed to be entirely due to the oxidation of biogenic precursors. The amount of gas-phase precursors available to form SOA via reactions with ozone are derived from several experimental observations (1) an average value for the amount of ozone lost in the canopy due to chemical reaction calculated from measured ozone flux data, (2) measurements performed in 2003 by the Proton Transfer Reaction Mass Spectrometry (PTRMS) that provide an average value of the concentration of very reactive biogenic volatile organic compounds oxidation products in the canopy, and (3) additional measurements performed using the PTRMS system in smog chamber experiments that indicate average yields from monoterpenes of approximately 20%. In combination, these observations provide a conservative lower limit for SOA yields from biogenic VOC oxidation. Difference between the calculated aerosol mass and estimated biogenic SOA that form due to biogenic emission reactions are attributed to competitive oxidation pathways. The results from the bounding analysis will be compared to measurements of organic aerosol mass collected at the site.

SPECIATION OF HETEROCYCLIC NITROGEN COMPOUNDS IN BIOMASS BURNING AEROSOLS USING TWO-DIMENSIONAL GAS CHROMATOGRAPHY-MASS SPECTROMETRY WITH HEART-CUTTING

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The development of a thermal extraction-two-dimensional gas chromatography-mass spectrometry (TE-GC-GC-MS) method (with heart-cutting) is described. The method is capable of identifying and quantifying nitrogen (N)-bearing organic species (e.g., pyrrole, pyridine, nitriles, and amines) in biomass burning aerosols. Pyrolysis of biofuel constituents is a likely formation pathway for these compounds. An evaluation of the TE-GC-GC-MS method proficiency confirms low carryover (< 1%), adequate recovery (84-100%), high reproducibility (< 9% RSD), picogram method detection limits, and a linear dynamic range spanning four orders of magnitude. Quantitative results are provided for 14 heterocyclic aromatic N substances that comprise 2% wt/wt of the total fine aerosol mass. The benefits of TE-GC-GC-MS versus conventional GC-MS methods for N heterocyclics in aerosols may depend on the matrix and the target N analyte concentration in that matrix. For the biomass burning aerosols examined in the present study, TE-GC-GC-MS reduces the unresolved complex mixture and detects organic N species not seen with conventional GC-MS techniques. Another advantage of TE-GC-GC-MS is that it adequately resolves the anhydro sugar (e.g., levoglucosan), alkanoic acid, and substituted phenol molecules in the biomass burning aerosol without the use of methylation or trimethylsilyl derivatizing agents.

DIRECT DETERMINATION OF LEVOGLUCOSAN AND ASSOCIATED SPECIES IN FINE PARTICULATE MATTER WITH THERMAL EXTRACTION-GC-GC-MS

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We describe a thermal extraction-two-dimensional gas chromatography-mass spectrometry (TE-GC-GC-MS) method with heart-cutting for the direct determination of levoglucosan (1,6-anhydro- β -D-glucopyranose) and other monosaccharide anhydrides (MAs) in fine particle matter (PM_{2.5}). The PM_{2.5} examined with the method was sampled from biomass smoke plumes and from the atmospheres of North American and African continents. The method fully separates levoglucosan from its mannosan and galactosan isomers. Levoglucosan accounted for as much as 7% of the mass in the atmospheric aerosols and its concentration range was 0.3-3.0 $\mu\text{g}/\text{m}^3$. Conventional solvent extraction-GC-MS and TE-GC-GC-MS measurements detect virtually identical levoglucosan concentrations in PM_{2.5} and agreed to within 2% on average. We show that TE-GC-GC-MS adequately resolves organic acids and substituted phenols in PM_{2.5} without the use of methylating or silylating agents. Finally, examples of how the technique reduces the unresolved complex mixture in the chromatograms and detects nitrogen heterocyclics are given.

PERFORMANCE OF A DIFFUSION DENUDER FOR THE ELIMINATION OF SAMPLING ARTIFACTS FOR CARBONACEOUS AEROSOLS AT THREE URBAN AND TWO FORESTED SITES IN EUROPE

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Mikuška et al. (2003) developed an annular diffusion denuder for removing volatile organic compounds (VOCs) and some oxidants (O_3 and NO_2) from the incoming air stream for low-volume (17 L/min) 47-mm diameter filter samplers. The denuder has since then been used and evaluated in several sampling campaigns in Europe. Here, we report on its performance in 3 winter campaigns (at Barcelona, Ghent, and Amsterdam) and 4 summer campaigns (the urban sites of Ghent and Amsterdam and the forested sites of K-pusztá, Hungary, and Hyytiälä, Finland). In all cases, a denuded $PM_{2.5}$ sampler (DQ1Q2) and an undenuded one (Q1Q2) were operated in parallel. Both samplers had two pre-fired 47-mm diameter Whatman QM-A quartz fibre filters in series. The collection time per sample was in all campaigns typically 24 hours and the duration of each campaign was about one month. The filters were analyzed for organic carbon (OC) and elemental carbon (EC) by a thermal-optical transmission technique (Birch and Cary, 1996).

The average OC concentrations, as derived from the first filter of Q1Q2, were lowest at the forested sites, i.e., $2.8 \pm 1.4 \mu g/m^3$ [N=26] at Hyytiälä and $3.4 \pm 1.7 \mu g/m^3$ [N=34] at K-pusztá, and they ranged from 3.9 to $6.9 \mu g/m^3$ for the campaigns at the urban sites. The average percentage OC on the second filter of Q1Q2, relative to the OC on the first filter, ranged from 10% to 18% for the summer campaigns (with the highest percentage obtained for K-pusztá) and from 4% to 11% for the winter campaigns. For the DQ1Q2 sampler, the mean percentage OC on the second filter, relative to the OC on the first filter, was for all sites lower than 5% and it was typically around 2% only.

Mader et al. (2003) have indicated that, if the positive artifacts (that is adsorption of VOCs to the filters) prevail for the first (front) filter in the undenuded samples and the negative artifacts (loss of semi-volatile organic compounds from the collected aerosol on the filters) prevail for the first filter in the denuded samples, artifact-free particulate OC data (OC_corr) may be obtained for the undenuded samples by subtracting the OC on the second filter from that on the first filter, while for the denuded samples artifact-free data may be obtained by adding the OC data of the first and second filters. Moreover, the data from the two sampler types should be the same after applying such correction. We applied this approach and calculated then for each sample pair the ratio of OC_corr for the first filter of Q1Q2 to OC_corr for the first filter of DQ1Q2 and averaged this ratio over all sample pairs from the same campaign. The mean ratios for OC_corr ranged from 0.97 to 1.17, whereas the same ratios for uncorrected OC ranged from 1.20 to 1.47. It may thus be concluded that the assumptions of Mader et al. (2003) were reasonably valid during all campaigns.

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MEASUREMENT OF CARBONACEOUS AEROSOLS WITH A SEMI-CONTINUOUS, REAL-TIME CARBON AEROSOL ANALYSIS INSTRUMENT AT THREE FORESTED SITES IN EUROPE

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A semi-continuous real-time carbon aerosol analysis instrument from Sunset Laboratory (Tigard, OR, USA) with a parallel-plate carbon filter denuder in the incoming airstream was used to measure carbonaceous aerosols in PM_{2.5} during field campaigns at three forested sites in Europe. The first campaign took place at the K-pusztá EUSAAR station, Hungary, from 24 May until 29 June 2006; the second campaign was at the state forest “De Inslag”, Brasschaat, Belgium, with a first part from 25 April to 13 July 2007 and a second part from 19 September to 12 November 2007; the third campaign took place at the SMEAR II station (also a EUSAAR site) in Hyytiälä, Finland, from 1 to 31 August 2007. At K-pusztá and Hyytiälä, a standard TEOM, with the filter heated at 50°C, was operated in parallel with the carbon instrument, for obtaining the particulate mass (PM) in PM_{2.5}. The time resolution of the carbon instrument was 1 hour at K-pusztá and in the first part of the campaign at Brasschaat; it was 2 hours in the second part of the campaign at this site; at Hyytiälä, it was varied from 1 hour to 4 hours, depending on the organic carbon levels. The real-time carbon instrument of Sunset Laboratory is based on the same principles as the lab instrument from the same company and makes use of a thermal-optical transmission technique to measure total carbon (TC) and to discriminate between thermal elemental carbon (EC) and thermal organic carbon (OC) (Birch and Cary, 1996). In addition, the real-time instrument provides data for optical EC (OptEC), which are obtained from the transmitted laser light (660 nm) intensity through the sampling filter. From the difference between TC and OptEC optical OC (OptOC) is then deduced. The hourly TC data at K-pusztá ranged from 0.3 to 12 µg/m³, with median of 2.6 µg/m³. Thermal EC and OptEC at this site were well correlated with each other, with a regression slope close to 1 and R² = 0.54. The sensitivity of the measurement for OptEC is substantially better than for thermal EC, so that the latter are not very reliable at low EC levels, as was the case at K-pusztá and especially in Hyytiälä. The average ratio of OptEC/TC for the K-pusztá campaign was 0.15±0.05. For the first part of the campaign at Brasschaat, TC ranged from 0.3 to 9.2 µg/m³ (median 2.5 µg/m³) and the average OptEC/TC ratio was 0.26±0.11; for the second part at Brasschaat, the range in TC was 0.4 – 14 µg/m³ (median 3.4 µg/m³) and the average OptEC/TC ratio was 0.36±0.12. At Hyytiälä, TC ranged from 0.15 to 8 µg/m³ (median 2.7 µg/m³), and the OptEC/TC ratio was, on average, 0.08±0.04. From a comparison of the OptEC/TC ratios at the three sites, it can be concluded that the SMEAR II site was least impacted by fossil fuel combustion aerosols and that the Brasschaat site was most impacted. The EC/TC ratio at Brasschaat is similar to that observed at Ghent and other urban sites in Europe (e.g., Viana et al., 2007).

Using 24-hour averaged data, both OC and the PM followed the air temperature at K-pusztá, with higher levels at higher temperatures. However, the high-time resolution dependence of the two components on temperature was quite complicated. During the warm period of the campaign (from 12 June 2006 on) there was clearly a tendency for opposite diurnal variation of OC and temperature. The higher OC levels during the night than during the day may be due to a combination of several reasons, including the build-up of a shallow atmospheric boundary layer during the night, the larger partitioning of semi-volatile organic compounds towards the vapour phase during the warm day, increased formation of SOA from condensable compounds during the cool night, and/or specific nighttime chemistry resulting in SOA formation.

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ONE-YEAR STUDY OF ORGANIC AND ELEMENTAL CARBON AT SIX SITES IN FLANDERS, BELGIUM

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Within the framework of the PM₁₀ chemical characterisation project “Chemkar”, quartz fibre filter samples were collected at six sites in Flanders and analyzed for the particulate mass (PM) and organic and elemental carbon (OC and EC). The sites were Houtem, Zelzate, Borgerhout, Mechelen, Aarschot, and Hasselt. They are roughly located along a west to east axis in Flanders, from near the French border to the middle of the province of Limburg, near the German border. Using the same site classification as Van Dingenen et al. (2004), Houtem can be considered a rural background site, Aarschot a near-city background site, and Mechelen and Hasselt urban background sites; Borgerhout is an urban traffic site and Zelzate an industrial site. The filters used were pre-fired 47-mm diameter Whatman QM-A quartz fibre filters. 24-hour samples were collected in parallel at the six sites every sixth day from 16 September 2006 until 11 September 2007. The filters were weighed to obtain the PM and analyzed for OC and EC by a thermal-optical transmission technique (Birch and Cary, 1996).

The PM time series for the six sites followed each other fairly closely; this was also the case for the OC time series, but much less for the EC time series. This suggests that the OC and the other major components of the PM originated rather from regional sources, whereas the EC levels were more determined by local sources. The coherence in the time series for the PM and OC was also reflected in the similarity of the yearly median concentrations (and interquartile ranges) for the six sites. The medians at Houtem, Zelzate, Borgerhout, Mechelen, Aarschot, and Hasselt for the PM were 26, 34, 35, 29, 26, and 27 $\mu\text{g}/\text{m}^3$, respectively, and for OC 2.7, 3.9, 4.5, 4.4, 3.6, and 3.8, respectively. For EC the relative difference between the medians was quite large, the median ranged from 0.39 $\mu\text{g}/\text{m}^3$ at Houtem to 1.77 $\mu\text{g}/\text{m}^3$ at Borgerhout. For EC there is likely a large contribution from automotive emissions at all sites. These emissions may also have provided a substantial contribution to the OC at most of the sites. The yearly median ratios of EC to total carbon (TC, with $\text{TC} = \text{OC} + \text{EC}$) ranged from 0.20 to 0.22 for four of the sites, it was 0.28 for Borgerhout and clearly lower (only 0.12) for Houtem. Even if we assume that the EC, which is a primary species, originates exclusively from traffic, it is impossible to estimate from the current data how much of the OC is due to traffic. This carbonaceous component has even at the urban sites certainly also other sources besides traffic; besides, a substantial fraction part of the OC is likely secondary. However, considering that the EC/TC ratio at Houtem is about a factor of two lower than at the other sites, it can certainly be stated that less than 50% of the OC at Houtem is derived from automotive emissions.

We also calculated the contribution of the carbonaceous aerosol to the PM. In this analysis we estimated the carbonaceous aerosol as the sum of 1.4 OC plus EC. The yearly median contributions of the carbonaceous aerosol to the PM were 16, 20, 24, 24, 22, and 24% for Houtem, Zelzate, Borgerhout, Mechelen, Aarschot, and Hasselt, respectively.

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MASS SIZE DISTRIBUTION OF ORGANIC CARBON AND THE PARTICULATE MASS DURING A 2007 SUMMER FIELD CAMPAIGN AT SMEAR II IN FINLAND

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An intensive atmospheric aerosol measurement and characterisation campaign was conducted during the full month of August 2007 at the SMEAR II station in Hyytiälä, Finland. As part of the activities, size-fractionated aerosol samples were collected with two cascade impactors, i.e., a 12-stage small deposit area low-pressure impactor (SDI) and a 10-stage microorifice uniform deposit impactor (MOUDI), which was extended with 3 nanoMOUDI stages. Separate collections were made during daytime (from 7:30 to 19:40 local time) and nighttime (from 20:20 to 6:40 local time). The two impactors were operated at ambient temperature and relative humidity (RH). The collection surfaces in the SDI consisted of pre-fired Pall quartz fibre filters and the impaction surfaces in the MOUDI of pre-fired aluminium foils. The SDI samples were analysed for organic and elemental carbon (OC and EC) with a thermal-optical transmission (TOT) technique (Birch and Cary, 1996), whereas the MOUDI aluminium foils were weighed at 20°C and 50% RH to obtain the particulate mass (PM). Besides the two cascade impactors, a DMPS was operated with 10-min time resolution to derive the number size distribution from 3 nm to 1 µm mobility diameter. The DMPS was deployed under dry conditions (RH <30%).

The mass of EC on the SDI stages was close to the detection limit of the TOT method and will therefore not be discussed. In Hi-Vol PM_{2.5} filter samples that were taken in parallel, EC could easily be determined and the EC/TC ratio (with TC = OC + EC) for these samples throughout the campaign was, on average, 0.060 ± 0.020 , indicating that the site was very little affected by fossil fuel combustion particles. The mass size distributions for OC and PM peaked in the accumulation size range, but there was also a clear coarse mode for both with peak at around 3–4 µm aerodynamic diameter (AD). Two distinct submicrometer modes, with peaks at about 0.3 and 0.7 µm AD, were clearly present for OC in the accumulation size range for the individual daytime SDI samples, whereas in the nighttime SDI samples the two modes seemed to have consistently merged into one broad accumulation mode. Two submicrometer modes have been observed before for several inorganic species in SDI samples (Ricard et al., 2002) and they were termed condensation and droplet modes for the lower and upper submicrometer modes, respectively. Ricard et al. (2002) attributed the droplet mode to cloud (or fog) processing. The droplet mode for OC may well be due to the same processing. It appeared from the analysis of the above-mentioned Hi-Vol PM_{2.5} filter samples that a very large fraction of the PM_{2.5} OC was water-soluble, on average, $63 \pm 7\%$. As to the broad accumulation mode during the night, this is likely due to hygroscopic growth of the OC. The RH increased to 80–100% during night, whereas it generally decreased to well below 60% during daytime. In the MOUDI size distributions for the PM, no distinct submicrometer modes could be discerned, but this is attributed to the fewer number of submicrometer stages than in the SDI. Both during day and night, the PM exhibited a broad submicrometer size distribution, but with peak at slightly larger diameter during night than during the day (i.e., at 0.45 µm AD versus 0.40 µm AD). For the dry volume size distributions derived from the DMPS there was no difference between the average daytime and nighttime distributions; both peaked at 0.25 µm mobility diameter. This is fully consistent with the difference between day and night mass size distributions for OC and the PM being caused by hygroscopic growth during the night.

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WATER-SOLUBLE ORGANIC CARBON IN PM_{2.5} AT SOME URBAN AND FORESTED SITES IN EUROPE

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PM_{2.5} aerosol samples were collected with a Hi-Vol dichotomous sampler during campaigns (of around one month) at two urban sites (Budapest, Hungary, spring 2002; Ghent, Belgium, fall 2003, winter and summer 2004, and winter 2005) and at three forested sites (Brasschaat, Belgium, summer 2007; K-pusztá, Hungary, summers 2003 and 2006; Hyytiälä, Finland, summer 2007). Double pre-fired Gelman Pall quartz fibre filters were used for all collections and the collection time per sample was 24 h for the campaigns in Ghent and typically 12 h in the other campaigns. The purpose of the double filters (front and back) was to assess the importance of artifacts in the carbonaceous aerosol collection. The filters were analysed for organic, elemental, and total carbon (OC, EC, and TC = OC + EC) with a thermal-optical transmission (TOT) technique (Birch and Cary, 1996) and for water-soluble OC with a Shimadzu TOC-V CPH analyser (Viana et al., 2006).

Table 1 gives the median concentrations (and ranges) in $\mu\text{g}/\text{m}^3$ for PM_{2.5} TC, as derived from the front filters, in the various campaigns and the means and associated standard deviations for various other parameters. EC on the back filters was insignificant for all samples. It appears that the percentage of the OC that is water-soluble is substantially higher for K-pusztá and Hyytiälä than for the two urban sites, whereas the value at Brasschaat is intermediate. This suggests that there was more secondary organic aerosol at the forested sites, which was presumably formed from the oxidation of biogenic volatile organic compounds. It is worth indicating that in a one-year study at several European sites (Yttri et al., 2007) no systematically larger WSOC percentages were found for rural sites than for urban sites. The percentages of WSOC on the back filter (relative to the front filter) are systematically higher than the corresponding percentages of OC. If we assume that the artifact is predominantly positive, this seems to suggest that the adsorbed volatile organic compounds are more water-soluble than the particulate OC.

Table 1: Medians and ranges (in $\mu\text{g}/\text{m}^3$) for TC and means and associated standard deviations for selected parameters during 9 campaigns.

Campaign	TC (Front filter)	EC/TC (Front filter)	%WSOC (of OC) (Front filter)	OC ratio Back/Front (%)	WSOC ratio Back/Front (%)
Budapest 2002	8.9 (3–23)	0.34 ± 0.12	36 ± 8	17.2 ± 4.2	28.4 ± 6.7
Ghent 2003	4.3 (2–17)	0.18 ± 0.08	35 ± 8	8.7 ± 2.3	16.1 ± 5.4
Gent 2004W	5.4 (2–12)	0.16 ± 0.08	38 ± 7	9.6 ± 2.8	17.1 ± 7.2
Gent 2004S	3.1 (1.5–5)	0.26 ± 0.08	43 ± 7	14.2 ± 2.3	21.5 ± 5.3
Gent 2005W	4.1 (1.1–20)	0.21 ± 0.12	43 ± 9	11.1 ± 3.6	18.0 ± 7.1
Brasschaat 2007	2.1 (0.8–8)	0.21 ± 0.09	51 ± 9	17.9 ± 4.8	23.8 ± 9.3
K-pusztá 2003	4.4 (2–7)	0.049 ± 0.014	61 ± 9	13.3 ± 4.3	19.3 ± 6.3
K-pusztá 2006	3.0 (1.1–7)	0.063 ± 0.030	57 ± 9	14.6 ± 4.4	18.6 ± 5.8
Hyytiälä 2007	1.8 (0.3–5)	0.060 ± 0.020	63 ± 7	16.8 ± 4.0	18.5 ± 5.2

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CHARACTERISATION OF ATMOSPHERIC CARBONACEOUS AEROSOLS IN PM_{2.5} AND PM₁₀ SIZE FRACTIONS AT TWO SITES IN TANZANIA

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This study was motivated by the fact that virtually no data for carbonaceous aerosols are available for Tanzania. Therefore, PM_{2.5} and PM₁₀ aerosol samples were collected at two sites in Tanzania during three campaigns (two wet and one dry season campaign) between May 2005 and May 2006. The sites were at Dar es Salaam (a kerbside) and at Morogoro (a rural site). PM_{2.5} and PM₁₀ filter holders with two pre-fired quartz fibre filters (front and back) in series were deployed. Depending upon the season and the location, either 24-hour collections or separate daytime and nighttime samplings were performed and the duration of the campaigns was either two weeks or one month (with one month used for the 2005 dry season and 2006 wet season campaigns). While a PM₁₀ sampler was operated in each campaign, a PM_{2.5} sampler was only deployed in the 2006 wet season campaign at Morogoro and in the 2005 dry season and 2006 wet season campaigns at Dar es Salaam. The samples were analysed for the particulate mass by gravimetry, for organic carbon (OC), elemental carbon (EC), and total carbon (TC = OC + EC) by a thermal-optical transmission technique (Birch and Cary, 1996), and for water-soluble organic carbon (WSOC) with a Shimadzu TOC-V CPH analyser (Viana et al., 2006).

At Morogoro, the back/front filter ratios for the PM₁₀ mass and OC were around 0.10 in the wet season campaigns and about 0.05 in the 2005 dry season campaign; at Dar es Salaam, these ratios were around 0.05 in the wet season campaigns and around 0.08 in the 2005 dry season campaign. If we assume that the data for the back filter are mostly due to positive artifacts (i.e., adsorption of volatile compounds), this all suggests that such artifacts were rather minor. At both sites, slightly over 80% of the PM₁₀ EC was in the PM_{2.5} size fraction; for OC, around 55% was in PM_{2.5}, and for the particulate mass, around 45% was in PM_{2.5} at Morogoro and somewhat less than 40% at Dar es Salaam.

At Morogoro the median levels of the PM₁₀ mass, as derived from the front filters, were 25, 47, and 14 $\mu\text{g}/\text{m}^3$ in the 2005 wet, 2005 dry, and 2006 wet season campaigns, respectively. Front filter TC accounted, on average, for 31%, 27%, and 33% of the front filter PM₁₀ mass in the 2005 wet, 2005 dry, and 2006 wet season campaigns. A larger fraction of the front PM₁₀ OC was water-soluble in the dry season (on average, $42 \pm 7\%$) than in the wet season campaigns ($36 \pm 4\%$ in 2005 wet and $31 \pm 8\%$ in 2006 wet). This is likely due to increased contribution from biomass burning and from secondary organic aerosol during the dry season. The OC at the Morogoro site is thought to originate from biomass and biofuel burning and from natural primary and secondary aerosols that originate from the vegetation. As far as biomass/biofuel burning is concerned, domestic biofuel burning, charcoal production and combustion, and agricultural waste burning are thought to prevail.

At Dar es Salaam, the medians for the PM₁₀ mass were 46, 62, and 44 $\mu\text{g}/\text{m}^3$ in the 2005 wet, 2005 dry, and 2006 wet season campaigns, respectively. TC made up around 33% of the PM₁₀ mass and about 28% of the PM₁₀ OC was water-soluble. The EC/TC ratio was much higher at Dar es Salaam than at Morogoro, i.e., 0.20-0.30 versus less than 0.10, which reflects the much larger impact from traffic at Dar es Salaam. Non-crustal, non-sea-salt K was used in combination with the OC data to apportion the OC at Dar es Salaam to traffic and charcoal burning. On average, 70% of the PM₁₀ OC was attributed to traffic and 30% to charcoal burning.

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BLACK CARBON AND ORGANIC CARBON DURING SMOCC: THE ABSORBING FRACTION OF BIOMASS BURNING AEROSOLS IN THE AMAZON BASIN

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Aerosol samples were collected in a pasture site in the Amazon Basin as part of the project LBA-SMOCC 2002 (*Large Scale Biosphere Atmosphere Experiment in Amazonia - Smoke Aerosols, Clouds, Rainfall and Climate: Aerosols from Biomass Burning Perturb Global and Regional Climate*) during the end of the dry season. A 13-stage Dekati low-pressure impactor (DLPI) was used to collect particles with diameters ranging from 0.03 to 0.10 μm . Gravimetric analyses were performed to obtain the aerosol mass concentrations collected on the DLPI aluminum substrates. The concentrations of carbonaceous species (total carbon (TC), elemental carbon (EC) and organic carbon (OC)) were determined using evolved gas analysis (EGA) and thermal-optical analysis (TOA). A light transmission method (LTM) was used to determine the mass concentration of black carbon (BC) or the absorbing fraction at 880 nm for the size-resolved samples.

During the dry period, due to the proximity of the fires to the sampling site, mass concentrations were higher for fine particles ($D_p < 2.5 \mu\text{m}$, $59.8 \mu\text{g m}^{-3}$) than for the coarse fraction ($D_p > 2.5 \mu\text{m}$, $4.1 \mu\text{g m}^{-3}$). The average TC concentrations were in the range of 24 - 64 $\mu\text{g of carbon m}^{-3}$. In terms of the particle organic matter (POM) and BC, the carbon fraction contributed with more than 90% of the total estimated aerosol mass. A comparison between the EC and BC concentrations generated from the EGA, TOA, aethalometer, and LTM showed that little variability in these concentrations is observed if water extraction and optical correction are performed. The size-resolved BC measured by the LTM showed a clear mode for D_p between 0.4 and 0.6 μm . Light absorbing particles in the range 0.1 to 1.0 μm exhibited strong wavelength dependence that diminished significantly after water extraction ($\lambda = 2.2$), but did not go down to 1.0, suggesting that still after water extraction there is OC contributing to the absorption of light. The size-resolved POM and BC concentrations showed that, in the fine fraction, these species have the same source (biomass burning) during the dry season. It is probable that the BC observed in the coarse is due to the formation of an internal mixture between soot carbon particles and other particles in the coarse mode and/or due to absorption of light by large particles (e.g., biogenic).

A NEW METHOD FOR THE REMOTE CHARACTERIZATION OF AIRCRAFT ENGINE EMISSIONS

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Type of Presentation Requested: Oral

The aim of this study was to capture and characterize plumes from commercial aircraft during landing and take-off (LTO) cycle under real world conditions.

A novel mobile measurement system, Plume Capture and Analysis System (PCAS), mounted in a four-wheel drive vehicle was used for aircraft engine emission measurements. The PCAS was positioned in the airfield 60 to 180 meters downwind of aircraft during different modes of ground level aircraft operation, including idling, taxiing, takeoff, and landing.

PCAS consists of a Plume Capture Device (PCD) which collects samples of the naturally diluted plume in a 200 L conductive membrane conforming to a defined shape, as well as particle and gaseous measurement instruments connected to the sampler, which provided real-time measurements of aircraft emissions simultaneously. Samples from over 280 aircraft movements were collected and analyzed in-situ for particulate and gaseous concentrations and for particle size distribution using a Scanning Particle Mobility Sizer (SMPS). Emission factors are derived for particle number, NO_x, SO₂, and PM_{2.5} for a widely used commercial aircraft type; including a range of Boeing and Airbus aircraft.

The practical advantages of the PCAS, include the capacity to perform well targeted and controlled emission factor and size distribution measurements using instrumentation with varying response times within an airport facility, in close proximity to aircraft during their normal operations.

Results from this study show that NO_x, and particle number emission factors are dependant on aircraft engine thrust level. Minimum and maximum emissions factors for particle number, PM_{2.5}, and NO_x emissions were found to be in the range of 4.16×10^{15} - 5.42×10^{16} kg⁻¹, 0.03-0.72 g.kg⁻¹, and 3.25-37.94 g.kg⁻¹ respectively for all measured airframes and LTO cycle modes. PM_{2.5} emission factors were highest during landing mode probably due to the presence of larger particles produced during landing as aircraft wheels touch the runway. According to International Civil Aviation Organization (ICAO), the thrust levels for taxi and idle operation modes are considered to be the same (7% of total thrust) [1]. However actual thrust level used during taxiing varies considerably given that taxiing aircraft involves acceleration and deceleration. Analysis of aircraft engine emissions during LTO cycle in this study show that aircraft thrust level is considerably higher during taxiing than idling mode.

This project was supported as a collaborative research agreement between Queensland University of Technology (QUT), and Brisbane Airport Corporation (BAC), Brisbane, Australia.

1. ICAO - International Civil Aviation Organization *Environmental Protection, Annex 16, Vol. II, Aircraft Engine Emissions, 2nd Edition*; Montreal, 1993.

MEASUREMENT OF PARTICLE SIZE DISTRIBUTION OF COMMERCIAL AIRCRAFT EMISSIONS

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Type of Presentation Requested: Oral

Measured size distribution of particles in the commonly used commercial aircraft exhaust, including a range of Boeing and Airbus airframes under real world conditions, are presented and discussed.

A mobile laboratory, developed and calibrated in International Laboratory for Air Quality and Health (ILAQH) at Queensland University of Technology (QUT), was used for real-time measurements of aircraft emissions. In order to maximize the size distribution measurement range, two Scanning Mobility Particle Sizers (TSI 3934 SMPS) were used for majority of size distribution measurements of submicrometer aerosols in the range of 4.45 to 710 nm [1]. The SMPS systems used in this study consisted of two different combinations of Electrostatic Classifier and Condensation Particle Counter (TSI EC 3071A/ TSI CPC 3010) and (TSI EC 3080/ TSI CPC 3025) covering 14.6 – 710 nm, and 4.45 – 157 nm respectively. Measurements were conducted in the airfield while the PCAS was positioned 60 to 180 meters downwind of aircraft during different modes of Landing and takeoff (LTO) cycle, including idling, taxiing, takeoff, and landing.

Size distributions obtained from commercial aircraft during different modes of LTO cycle show that the majority of the particles were found to be in the range of 4 to 100 nm in diameter in all cases.

A very distinct nucleation mode was observed in all particle size distributions ($CMD \approx 13$ nm), except for A320 aircraft during taxiing and landing. This can be attributed to A320 engine properties and combustion, as measurement conditions were similar for all types of aircraft. The observed nucleation mode consists of particles with diameters smaller than 30 nm which have the highest number concentrations in all cases.

The accumulation mode between 40 and 100 nm, peaked at ~ 60 nm, was more pronounced in particle number size distributions obtained during takeoff in comparison to other aircraft operating modes. The accumulation mode was most apparent in particle mass size distributions in all cases.

In this presentation, contributions of nucleation and accumulation modes in aircraft engine plume particle size distributions to $PM_{2.5}$ concentrations at each phase of LTO cycle will also be presented.

This project was supported as a collaborative research agreement between Queensland University of Technology (QUT), and Brisbane Airport Corporation (BAC), Brisbane, Australia.

1. TSI Incorporated <http://www.tsi.com>

DIESEL PARTICULATE CHARACTERISATION IN THE MARITIME ENVIRONMENT.

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Abstract

Measurements of diesel particulate emissions from maritime sources are rare, but this form of transportation produces significant personnel exposure in ports and at sea to shipboard personnel. However, unlike the land environment, the nautical environment enables the measurement of diesel particulate matter (DPM) without the complications of interference from other combustions sources.

Continuous measurements of DPM were conducted in a conventional diesel-electric submarine. They consisted of particle size distribution and adsorbed polycyclic aromatic hydrocarbons using self logging instruments. In addition quartz and Teflon filter samples were collected for chemical speciation.

Quartz filters were used in the determination of elemental carbon (EC), organic carbon (OC) and total carbon (TC) using a thermal-optical method prescribed in NIOSH Method 5040. Carbon speciation results were compared with the IMPROVE method developed by the Desert Research Institute, NV, USA. In addition, the effect of size selective quartz filter samplers was investigated. Teflon filters were used to chemically characterise the soluble inorganic components of particulate matter and for validation of diesel exhaust particle mass concentrations.

EC, TC and DPM were found to conform with the requirements defined for exposure and risk assessments by the American Council of Government Industrial Hygienists, National Institute for Occupational Health and Safety and the US Mine Safety and Health Administration.

HISTORICAL BLACK CARBON CONCENTRATIONS AND DEPOSITION RATES FROM ICE CORES

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Black carbon (BC) results from biomass and fossil fuel combustion and is an important climate forcing agent. While little is known about emission or deposition histories, BC aerosols alter the chemical and physical properties of the atmosphere and even minute amounts when deposited to highly reflective surfaces such as snow can significantly lowers albedo.

Recent analytical developments mean that high-time resolution historical records of BC concentration in precipitation and deposition rates can be developed from ice cores. The first application of this method showed that BC concentrations and deposition rates varied at seasonal to decadal time scales in central Greenland precipitation during the 215 year period from 1788 to 2002. Comparisons to elemental and chemical source tracers measured in the same ice core suggested that boreal forest fires were the primary source of BC prior to North American industrialization in the mid-19th century and during summer throughout the 215 year record. North American industrial emissions (primarily coal burning) during the period 1850 to 1951 resulted in as much as a seven-fold increase in BC concentration, with most of the increase occurring in winter when preindustrial concentrations were generally low. The sharp drop in ice-core BC observed after ~1951 was attributed to a shift from coal to oil and gas burning in North America consistent with independent emissions estimates.

This first ice core record characterizes historical levels and sources of BC in central Greenland. Unlike well-mixed greenhouse gases, however, atmospheric lifetimes of BC and other aerosols are short so more ice core records are needed to fully understand spatial and temporal variations in BC. We present newly developed historical records of BC concentrations and deposition rates from a number of polar and alpine ice cores and use comparisons to source tracers to evaluate sources of BC at the ice core sites over recent decades and centuries.

Composition and properties of aerosol formed in the photo-oxidation of a range of terpenes at atmospherically-reasonable concentrations in a heavily instrumented simulation chamber

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It is well established that tropospheric oxidation of organic compounds plays a central role in ozone generation and may lead to secondary organic aerosol (SOA) component formation. Approximately 90% of organic material emitted globally is estimated to originate from biogenic sources, with almost half of all reactive biogenic volatile organic compounds (BVOC) emitted from tropical and sub-tropical forests. Observational studies indicate that biogenic SOA (BSOA) dominates remote aerosol organic carbon concentrations. Aerosol Couplings in the Earth System (ACES) is an integrated research project, funded under the UK NERC APPRAISE directed programme aiming to reduce uncertainties in fundamental understanding of tropical BSOA formation and the subsequent impact on atmospheric composition, through coordinated chamber studies, field studies, process model development, and application of atmospheric models of chemistry and transport to assess coupling and feedbacks in the Earth system.

We will present results from chamber experiments carried out within ACES WP1 aiming to improve our mechanistic understanding of secondary organic material formation and to provide evaluation data for the near-explicit scheme for the oxidation of terpenes under development within WP3 extending the Master Chemical Mechanism (MCM). The biogenic species currently included in the MCM are isoprene and α - and β -pinene. With the intention to couple the gaseous oxidation mechanism to an explicit model for the dynamic evolution of the aerosol microphysics within the chamber, it was decided to develop the degradation mechanisms for five further biogenic species: limonene, α -terpinene, myrcene, β -caryophyllene and linalool. Their choice was informed by a survey of dominant cuvette-measured emissions of reactive BVOCs from the most prevalent Dipterocarpaceae and Euphobiaceae found at the Danum Valley Nature Reserve, Borneo; the location of the field measurements within ACES WP2.

The experiments were carried out in the new photochemical aerosol chamber at the University of Manchester. The chamber comprises an 18 m³ FEP Teflon bag operating at a slight overpressure, minimising contamination from laboratory air. A bank of halogen lamps and a 6 kW Xenon arc lamp provide illumination and air conditioning between the enclosure and the bag removes unwanted heat. Clean, dried and re-humidified air with controlled initial seed aerosol, parent VOC and NO_x loading is introduced before illuminating the bag and controlling the temperature. We will present results from photo-oxidation of a subset of the target BVOCs under an extensive set of experimental conditions with a particular focus on reduced (e.g., 10 ppb) parent VOC mixing ratio experiments. The effect of nucleation vs partitioning will be illustrated through contrast of results with and without the use of both wet and dry seed aerosols.

The instrumentation payload used in the investigation includes a Chemical-Ionization Reaction Time-of-flight Mass Spectrometer (CIR-TOF-MS) from the University of Leicester for gaseous VOC / OVOC identification and quantification, high resolution time-of-flight aerosol mass spectrometer (ToF-AMS) for realtime broad chemical aerosol characterisation, aerosol sizing, hygroscopicity and cloud activation behaviour by a range of aerosol probes (DMPS, HTDMA and CCN counter) all at the University of Manchester and filter sampling for analysis by LC-IT/MS and GCxGC-TOF/MS at the University of York. This payload has allowed composition determination and characterisation of a wide range of microphysical properties and potential atmospheric impacts which will be presented.

CHARACTERIZATION OF EMISSIONS FROM THE LABORATORY COMBUSTION OF WILDLAND PLANT SPECIES

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Biomass burning is a major source of organic particulate emissions to the atmosphere. Fires are highly localized in time and space and strongly affect regional air quality and climate. We performed a series of laboratory-based biomass burning experiments to characterize emissions from fuels frequently consumed in wildland and prescribed fires in the western and southeastern United States. The experiments were performed at the Fire Science Laboratory in Missoula, Montana. We measured aerosol composition, size, wavelength dependent light scattering and absorption, extinction, hygroscopic growth, cloud condensation nuclei activity, ice nucleation behavior, and emissions factors for trace gases (CO_2 , CO , C_{1-4} hydrocarbons, NO , NO_2 , NH_3 , HNO_3 , O_3 and SO_2). Emissions of carbon containing gases and particles were primarily a function of modified combustion efficiency, which describes the relative roles of flaming versus smoldering combustion, in determining the nature of the integrated emissions. Emissions of inorganic gases and particles depended more strongly on fuel type than on fire behavior. The composition of aerosols emitted by the burns ranged from organic carbon (OC) dominated particles to mixtures containing OC, elemental carbon (EC), and inorganic compounds in approximately equal proportions. Aerosol interactions with water depended most strongly on aerosol inorganic content—governed by fuel composition—whereas aerosol optical properties depended most strongly on OC/EC ratios—governed by combustion behavior. The large number and wide range of fuels and fuel components we tested provided a broad range of combustion behavior and corresponding smoke properties. Some fuels were dominated by smoldering combustion and produced weakly absorbing and hygroscopic aerosol dominated by OC. Other fuels were dominated by flaming combustion and produced light absorbing, hygroscopic aerosol dominated by EC and inorganics.

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THE LIGHT ATTENUATION SPECTRAL DEPENDENCE OF ORGANIC CARBON EMITTED BY BIOMASS BURNING

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We analyzed filter samples to determine the role of organic and elemental carbon emitted by biomass burning in visible and near-UV light attenuation using a UV-VIS diffraction grating spectrometer, thermal-optical analysis (TOA) techniques, and a variety of chemical extraction and analysis methods. The laboratory biomass burning experiments were performed at the Fire Science Laboratory in Missoula, Montana. A large range in elemental-to-total carbon ratios was observed, reflecting the variety of fuels and combustion conditions during the burns. Organic carbon (OC) in some samples, particularly those dominated by smoldering-phase combustion, played a significant role in visible and near-UV light attenuation. A power-law fit was used to quantify the wavelength dependence of attenuation, yielding the Angstrom attenuation exponent (α). Angstrom attenuation exponents ranged from ~ 0.7 for flaming phase- and elemental carbon (EC)-dominated fuels to ~ 3.5 for smoldering phase- and OC-dominated fuels. We relate α to combustion conditions, fuel types and EC/TC ratios to develop an approach for modeling this wavelength dependence of absorption in atmospheric models. A simple two-component model featuring strongly light absorbing, but weakly wavelength dependent black carbon and weakly light absorbing, but strongly wavelength dependent organic carbon reproduced the attenuation–wavelength relationships observed for bulk samples. We compare filter-based measurements of light attenuation to light absorption measured using photoacoustic spectrometers to examine potential filter-based measurement artifacts and show that filter-derived Angstrom attenuation exponent measurements agree with photoacoustic-derived Angstrom absorption exponents.

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SOURCE CONTRIBUTIONS TO FINE AND QUASI-ULTRAFINE ORGANIC CARBON IN THE LOS ANGELES-LONG BEACH HARBOR AREA

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The Los Angeles - Long Beach harbor is the busiest port in the US, and its surrounding area has one of the most polluted and complex atmospheres in the US, since it is affected by multiple PM sources. A detailed study of ambient particulate matter in this area was carried out during two different seasons. Size segregated particulate matter (quasi-ultrafine and accumulation mode) were collected at seven sites during a cooler period of higher air stagnation (March-May) and a warmer period of high photochemical activity (July-September) in 2007. Four of the sites were located within the communities of Wilmington and Long Beach, two sites were located at background areas in the harbor of Los Angeles and Long Beach, respectively, and one site was set near downtown Los Angeles, considered as a typical urban area. The collected PM samples were analyzed for organic carbon (OC), elemental carbon (EC), organic species, inorganic ions, water soluble and total elements. A comprehensive comparison was made between the two different seasons. Preliminary results showed higher levels of particulate sulfate, ammonium and octadecanoic and hexadecanoic acids in warmer season due to higher photochemical formation.

In order to identify and quantify the sources of OC, a source apportionment analysis was carried out using Chemical Mass Balance (CMB). Sources included in the model are: light duty vehicles (LDV), heavy duty vehicles (HDV), road dust (RD) (only for fine PM fraction), biomass burning (BB) and ship emission (SH), being then the first source apportionment study including vessel emissions. Preliminary results for winter showed that the addition of LDV, HDV and RD account for more than 60% of total fine OC, whereas ship emissions contribution is lower than 5% of total fine OC at all sites. This clearly indicates that organic matter in the study area is dominated by the vehicular sources despite the proximity of the studied communities to the largest US harbor.

A new instrument for measuring the mass, size, and chemical composition of soot containing particles

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Recent field and modeling studies highlight the substantial effects that carbonaceous aerosols may have on the earth's climate. The black carbon (BC) fraction has particularly important implications for climate, as it is a strong absorber of visible light and has substantial anthropogenic emission sources, and plays important roles in governing the optical properties of atmospheric aerosol. The estimated direct radiative effects of BC particles may be the second-most important contributor to global warming after the absorption of CO₂. In addition, absorption of solar radiation by BC-containing aerosols changes the vertical temperature profile of the troposphere, thus potentially affecting cloud coverage and large scale circulation.

Complete characterization of carbonaceous particles, including both the BC and organic mass (OM) components, is important for our understanding of the relationship between anthropogenic activity and the earth's climate. *In situ* techniques for the measurement of the chemical composition, mixing state, size distribution, and atmospheric transformations of carbonaceous particles are essential. Current black carbon particle instruments rely on either absorption measurements, for which the mass specific absorption coefficients are not well known, or the thermal conversion of particulate carbon to gas-phase CO₂ (Thermal Optical Analysis), which are inhibited by uncertain methods for elemental-organic carbon separation. A promising instrument for black carbon particulate mass measurements is the Droplet Measurement Technology (DMT) Single Particle Soot Photometer (SP2) instrument that measures soot particle incandescence, but provides no direct chemical information.

We are developing a new, real-time instrument for measuring the mass, size, and chemical composition of black carbon containing particles. This instrument combines SP2 continuous intracavity Nd:YAG laser (1064 nm wavelength) technology within the successful Aerodyne Aerosol Mass Spectrometer (AMS) instrument. The new instrument, SP2-AMS, utilizes the laser-induced heating (incandescence) of absorbing soot particles to vaporize both the coatings and elemental carbon cores within the ionization region of the AMS, providing a unique and selective method for measuring the mass and size of the refractory carbon cores (i.e., black carbon mass), and the mass, size, and chemical composition of any coating material (e.g., organics and inorganics) via standard 70 eV electron impact time-of-flight mass spectrometry.

We report results which demonstrate the utility of this technique for a variety of particles with and without black carbon cores, with and without various coatings. These measurements clearly show that the method is sensitive only for particles containing an absorbing component. The results also show that the mass spectrometric signals vary linearly with the amount of the black carbon and the condensed species mass. This allows for the identification and quantification of the chemical composition (refractory and nonrefractory) of absorbing particles with the goal of tracking and characterizing primary combustion particles as they are processed and transported in the ambient atmosphere.

PHOTOACOUSTIC AND AETHALOMETER MEASUREMENTS OF AEROSOL LIGHT ABSORPTION IN THE PRESENCE OF SECONDARY ORGANIC AEROSOL: MEXICO CITY, LAS VEGAS & RENO NEVADA, AND THE DOE ARM SITE IN OKLAHOMA

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Dan Lack and coworkers have recently documented a systematic bias in filter-based measurements of aerosol light absorption using the PSAP instrument when secondary organic aerosols (SOA) are present (Houston Texas study). Aerosol mass spectrometer measurements confirm the presence of SOA. We see little evidence of a systematic bias in our comparisons of aerosol light absorption measurement with our photoacoustic instruments operating at 532 nm and with multi-wavelength aethalometers in Mexico City and Las Vegas Nevada where in both cases SOA abounds. Possible explanations in the discrepancy include, but are not limited to, that the optics of the filter media in the PSAP and aethalometer are substantially different, that the SOA giving rise to the Houston result is chemically different than that present in Mexico City, and that humidity plays a direct or indirect role through its impact on photochemistry. A review of our previous PSAP and photoacoustic measurement comparisons for Reno (no bias detected) and the DOE ARM site in Oklahoma (strong bias detected) will also be given.

OPTIMIZED SEPARATION OF OC AND EC FOR RADIOCARBON-BASED SOURCE APPORTIONMENT OF CARBONACEOUS AEROSOL

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Radiocarbon is a powerful tracer that enables discrimination between fossil and non-fossil sources of carbonaceous aerosol. The former fraction includes ^{14}C -depleted substances, e.g. from traffic emissions, whereas the latter contains material on the contemporary ^{14}C level, e.g. from biomass-burning and biogenic emissions. The carbonaceous aerosol divides into organic carbon (OC) and elemental carbon (EC) fractions, which exhibit very different chemical and physical properties and are not influenced by the same sources. Therefore, isolating them so as to study their radiocarbon content separately appears of major interest.

This separation, which relies on the difference of volatility and chemical reactivity of both fractions, remains a challenge. On the one hand, OC is liable to char during its volatilization process, thus leading to the loss of a class of compounds for OC samples and to a contamination of the EC fraction. On the other hand, the thermal boundary between removal of OC alone and volatilization of a mixture of OC and EC is blurred and appears to be lowered by the presence of inorganic catalysts in the sampled aerosol or in the filter composition.

Consequently, an optical monitoring of the sample combustion is required for better understanding of those charring and co-volatilization processes in order to minimize their impact on ^{14}C measurements. We present current investigations on an adaptation of the sample preparation procedure described in Szidat et al. (2004) to a thermo-optical transmission device (Sunset EC/OC analyzer) running under pure oxygen. In this device, the CO_2 produced by volatilization of the different fractions during analysis is recovered and directly injected into an Accelerator Mass Spectrometer for radiocarbon analysis, which reduces the time of analysis. We discuss the development of optimized separation of the main fractions of carbonaceous aerosol using ambient aerosol samples.

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APPLICATION OF THE MINIMUM OC/EC RATIO TO THE SOURCE APPORTIONMENT OF ORGANIC CARBON IN PM_{2.5} AND PM₁₀ AEROSOLS: EVALUATION OF 15 YEARS OF MEASUREMENTS IN EUROPE

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The origin of its carbonaceous component is one of the, not yet completely clarified, main questions relating to the atmospheric aerosol. Direct emissions from fossil fuel combustion, or biomass burning, and secondary production from anthropogenic, or natural, gaseous precursors, are usually considered the principal sources of particulate aerosol carbon. Several methodologies have been applied to quantitatively source apportion the carbonaceous aerosol, including utilization of tracers, such as ¹⁴C, fine potassium and levoglucosan, but none of them is perfect because of factors such as cost or highly variable emission factors.

One of the older methodologies applied in carbonaceous aerosol source apportionment is based on minimum ratios of OC/EC concentrations, usually obtained in urban areas, in conditions of low photochemistry in winter. Minimum ratio values have been used to indirectly calculate secondary OC, although the methodology has been subjected to criticism because of a number of possible interferences.

Here we defend that, taking into account the limitations of alternative methodologies, the (OC/EC)_{min} ratio methodology can be a reasonable means of estimating the contribution of fossil fuel combustion (road transport mainly) to primary particulate OC, if applied with precaution in proper situations. This methodology, in association with complementary methods permits a more precise evaluation of carbonaceous aerosol sources and processes formation.

Fifteen years of OC and EC measurements in Europe, using our home made thermal-optical transmission method, provided a data set of size segregated, PM₁, PM_{2.5} and PM₁₀ OC and EC measurements in a variety of conditions (road tunnel, kerbside, urban, rural, marine and remote), during winter and summer, that was used to estimate the stability and variety patterns of OC/EC minimum ratios.

The data set permits to observe that (OC/EC)_{min} ratios happen for urban conditions in winter, with values linearly decreasing with increasing average concentrations of EC. This pattern can be attributed to a higher fractional contribution of regional secondary OC in occasions when EC pollution levels are lower. The minimum ratios of OC/EC are higher in PM₁₀ than in PM_{2.5} as result of the different size distributions of OC and EC.

With basis on OC/EC minimum ratio patterns and values of OC/EC ratios in road tunnel measurements it is possible to determine appropriate (OC/EC)_{min} ratios that can be applied to estimate the contribution of primary fossil fuel combustion to the PM_{2.5} and PM₁₀ aerosol OC loading.

PARTICULATE CARBON IN PRECIPITATION AT EUROPEAN RURAL/BACKGROUND SITES

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Current understanding on the cycling of carbonaceous aerosol particles is far from complete and one of the lesser known components of the cycle is wet deposition, which is known to be a key process at removing these particles from the atmosphere. To date, the number of studies dedicated to the measurement of particulate carbon in precipitation is very scarce. As a result, the spatial coverage of wet deposition data is restricted to a few scattered locations in Europe, North America and Africa. This paucity of information has been pointed as one relevant limitation to validate global models that simulate transport and concentration of atmospheric particulate carbon and consequently is affecting predictions of anthropogenic forcing on climate.

The particulate carbon content of precipitation was investigated in samples collected at five background sites distributed along a west-east European transect, from the Azores islands, in the North Atlantic Ocean, to the Hungarian plains, in central Europe. Sampling was performed on an event basis and the particulate carbon content was concentrated on quartz filters for the subsequent analysis by a thermal optical method in order to differentiate between the elemental carbon (EC) and water insoluble organic carbon (WIOC) fractions. The average concentrations were in the range of $2.8 \pm 4.3 \mu\text{gC L}^{-1}$, at the Azores, to $28 \pm 38 \mu\text{gC L}^{-1}$, at the inland site of Schauinsland (Germany), for EC, and in the range of $98 \pm 56 \mu\text{gC L}^{-1}$, at the coastal site of Aveiro (Portugal), to $358 \pm 194 \mu\text{gC L}^{-1}$, at the continental site of K-Pusztá (Hungary), for WIOC. The results are discussed in terms of factors affecting the spatial distribution of particulate carbon, such as emissions from surrounding areas and prevalent meteorological conditions. EC was a minor contributor to total particulate carbon in rain and snow samples. This was particularly relevant at the remotes sites, where the average EC content was below 6.5%, in line with a negligible impact of anthropogenic sources of pollution. The EC and WIOC scavenging ratios were estimated and compared with that of sulphate, also evaluated at the same sampling sites. The results indicated that EC is removed from the atmosphere by wet deposition less efficiently than WIOC, and in turn this species is removed less efficiently than sulphate.

Carbonaceous aerosols in urban and high-altitude environment of north-India

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Anthropogenic activities, biomass burning and fossil fuel emissions in south Asia are gaining significant attention for contributing atmospheric carbonaceous species (EC, OC), which in turn have potential to cause substantial impact on the regional climate and hydrological cycle. Both these species are emitted from the same sources in varying proportion, but with characteristically different physical, optical and chemical properties.

Our systematic study, by sampling through a network of stations, provides first data set on atmospheric abundances of EC and OC over north-Indian region and suggest that total carbonaceous aerosols ($TCA=1.6*OC+EC$) contribute significantly to the particulate mass (PM) at urban locations (about 30-35% of PM). Over high-altitude sites, TCA is the second largest contributor (~15-25% of PM) after mineral dust; with EC contribution ranging from 2 to 5% of PM. The OC/EC ratios (Table 1), except at Jaduguda, are relatively high compared to those over urban sites reported in the literature (OC/EC ~ 2 to 3). The higher EC emission from neighboring coal-mines is a likely cause for lower OC/EC ratio at Jaduguda (rural site). The systematically high OC/EC ratios, together with lower EC concentrations at urban and high-altitude sites are attributed to relative dominance of both primary and secondary organic carbon (OC and SOC) derived from biomass burning (crop waste). On average, contribution of SOC, calculated from minimum OC/EC ratio method, is about 15-20% of OC at high-altitude sites and is ~30-35% at urban locations. The large scale spatial and temporal variations in OC and EC warrant long-term continuous measurements using ground-based network in order to understand net aerosol forcing effect at the surface, close to their source regions.

Table 1: Abundances of carbonaceous species (EC, OC) and OC/EC ratios from different geographical locations in north-India

<i>Location</i>	<i>Lat</i> ° N	<i>Long</i> ° E	<i>Sampling period</i>	<i>Av. EC</i> $\mu\text{g m}^{-3}$	<i>Av. OC</i> $\mu\text{g m}^{-3}$	<i>OC/EC ratio</i>
High-altitude						
<i>Manora Peak</i>	29.4	79.5	2005-06	1.3 ± 0.7	10.3 ± 4.2	8.6 ± 2.8
<i>Mount Abu</i>	24.6	72.7	2005-06	0.5 ± 0.5	3.7 ± 2.4	6.1 ± 2.0
Urban						
<i>Hisar</i>	29.2	75.7	Dec-04	3.8 ± 1.4	33.0 ± 17.9	8.5 ± 2.2
<i>Kanpur</i>	26.5	80.3	Jan 06-June 07	3.2 ± 2.4	18.1 ± 10.9	5.7 ± 3.2
<i>Allahabad</i>	25.5	81.7	Dec-04	6.2 ± 2.0	49.0 ± 14.1	8.1 ± 1.7
Rural						
<i>Jaduguda</i>	22.5	85.7	Dec-04	11.6 ± 2.0	35.3 ± 7.1	3.1 ± 0.6

A NEW INSTRUMENT FOR NEAR-REAL TIME SIZE-RESOLVED ORGANIC CARBON MEASUREMENT

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Abstract:

Real time size distribution and size-resolved chemical composition measurements are essential for effective characterization of ambient aerosol. The currently available instruments are large in size, expensive, and often complicated in operation. Towards development of a compact instrument for size-resolved submicron particle composition studies, a new instrument design is presented. This instrument builds on the design of the Miniature Electrical Aerosol Spectrometer (MEAS, Ranjan and Dhaniyala, 2007, 2008). The MEAS design is composed of three sections: a charging section; Electrostatic Precipitator (ESP) section; and classification section. The particles are charged in the classification region using a bipolar/unipolar charger and sent to the ESP section where charged particles are sent through a parallel channels, spaced ~1mm apart. A potential difference is applied to capture charged particles in all ESP channels except one, through which charged particles are sent to the classification region. In the classification region, charged particles migrate due to an applied electric field and are collected on plates. The position of the collection plate and the magnitude of the applied voltage determine the particle size collected on the plates.

Current research has focused on extension of MEAS for composition monitoring. Aerosol particles ($D_p < 500\text{nm}$) over a narrow size range are collected on metallic plates in c-MEAS. Underneath the collection plates, ultraminiature heaters and heat sensors (Minco Inc.) are located to heat the plates to selected temperatures to volatilize the collected particles and the resultant sample is analyzed by gas analyzers at the MEAS exit. Particle vapor follows a thin pathline depending on the Archimedes Number (Ar) within the instrument. Optimum flow rate is obtained with minimum Ar in order to dampen the effect of free convection, which results in the unwanted flow circulation in the system. The

plates are heated from the last plate downstream of the flow in order to avoid the mixing of the particle vapor from one collection plate to the other. Numerical results suggest that heating under appropriate conditions of Ar will enable extraction of volatile species without loss to the walls.

Offline comparison of cMEAS with MOUDI has promising results, which stresses on the potential for cMEAS as a high resolution organic carbon distribution measurement instrument. cMEAS has been used for diesel exhaust and lawnmower exhaust organic carbon fraction measurement using Sunset/DRI carbon analyzer as well as with a novel MEMS based hydrocarbon sensor downstream of the instrument.

Gas detectors downstream of c-MEAS can be used for quantitative information on the volatilized species. A CO₂ NDIR sensor will be integrated for measurement of organic carbon volatilized from the size-segregated samples. A comparison of cMEAS performance against that of the Sunset EC/OC will be presented. Also, measurements of the size dependent high-volatile OC in ultrafine diesel emissions will be presented.

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MODELING SOOT AGING WITH A STOCHASTIC PARTICLE-RESOLVED AEROSOL MODEL

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The mixing state of atmospheric aerosol particles is of crucial importance for assessing their macroscopic impact, since it governs their chemical reactivity, cloud condensation nuclei activity and radiative properties. A prominent example for this is soot, which can be present in the atmosphere in external as well as in internal mixture. To represent soot and its impacts in atmospheric models, the transfer of soot from external to internal mixture, called “aging”, needs to be represented adequately.

However, tracking the mixing state in conventional aerosol models requires treating a multidimensional size distribution, which is computationally prohibitive. Therefore current models adopt certain simplifications, which usually translate into the assumption of an internal mixture within one mode or size section. The uncertainties associated with this assumption, which artificially ages freshly emitted particles instantly, are not well quantified.

In this study, we present a new approach, the stochastic particle resolved model PartMC-MOSAIC, which explicitly resolves the composition of individual particles in a given population of different types of aerosol particles, and accurately tracks their evolution due to emission, dilution, condensation and coagulation. PartMC-MOSAIC is applied to an idealized urban plume case to simulate the evolution of urban aerosols of different types due to coagulation and condensation. For this urban plume scenario we quantify the individual processes that contribute to the aging of the aerosol distribution, illustrating the capabilities of our model approach. We present a composition-based definition and a CCN-based definition of aging. The results show that depending on how we define “aging”, the aged soot fraction evolves differently in time. This highlights that there is no single aging criterion and that application-dependent measures of aging must be used.

SEASONAL VARIATIONS OF HIGHLY TIME-RESOLVED ORGANIC COMPOUNDS CONCENTRATIONS OF PRIMARY AND SECONDARY NATURE DURING THE BALTIMORE PM_{2.5}-SUPERSITE STUDY

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Most of the knowledge about the nature of ambient organic compounds associated with airborne fine particulate matter is obtained from integrated sampling of 24 hours or longer. While major insight has been obtained on the average composition of airborne carbonaceous aerosol matter, little is known about diurnal changes in concentrations due to the interplay of meteorology with local sources and pollutant transport from distant source regions. Likewise, the impact of atmospheric chemistry on the composition of organic aerosol is mainly unknown or limited to smog chamber experiments.

Here, a specially designed sampling system was deployed during the 2002-2003 Baltimore PM-Supersite Study to collect PM_{2.5} on filters and PUFs with a 3-hourly resolution for three weeks during summer and another three weeks during winter. From the sample sets, a total of four weeks for summer and winter were subjected to chemical analysis. Over 100 individual compounds including homologues series of n-alkanes, n-alkanoic acids, n-alkenoic acids, n-alkylcyclohexanes, hopanes, PAHs, oxy-PAHs, levoglucosan, resin acids, syringyl-moieties, aromatic and aliphatic dicarboxylic acids, secondary biogenic compounds, sterols, tris(2,4-di-tert-butylphenyl)phosphate and others were quantified.

For primary organics, no repeatable diurnal concentration patterns on a day to day basis are observed as one would expect if major local sources such as vehicular traffic would be isolated from nearby or more distant source regions. In contrast, averaging daily 3-hourly ambient concentrations reveal ambient diurnal patterns that relate to diurnal emission patterns of major source classes. With the increased time resolution, short-term release of pollutants from a temporary source can also be detected. For example, for a two day period, even carbon numbered higher molecular weight n-alkanes, indicators for plastic waste burning, have been measured at substantially elevated concentrations together with the locally prevailing meteorology, allowing pinpointing possible source regions. Another surprise is the substantial depletion of unsaturated fatty acids during the summer and the pronounced diurnal concentrations variations for these compounds during day and night in winter. Key biogenic secondary organic compounds have been detected as well, and their ambient concentration levels increase during the night when the relative humidity levels increase and chemical formation is favored.

STABLE ISOTOPE RATIOS OF WATER SOLUBLE ORGANIC AEROSOLS SEPARATED BY SIZE EXCLUSION CHROMATOGRAPHY

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Although many sources of organic aerosols have been identified, fundamental questions regarding ambient organic aerosol concentration and lifetime remain (e.g., secondary aerosol formation, cloud droplet nucleation). It can be difficult to infer aerosol sources, particularly of background (i.e., aged) aerosols, and of the high-MW component ("HULIS") of aerosols. The stable isotope ratios ($\delta^{13}\text{C}$) of organic aerosols have been used to distinguish between sources, with lighter values (-30 to -25‰) interpreted as having originated from fossil fuel combustion and biogenic emission, and heavier values (-25 to -20‰) indicating a marine or biomass burning source. Most published measurements were of either total suspended particulates or $\text{PM}_{2.5}$, however, and it is unknown to what extent these fractions differ from submicron (which may contain relatively less cellular material and thus be more representative of secondary formation). We report stable isotope ratios for submicron organic aerosols collected at a variety of sites, ranging from marine to polluted to background continental. Bulk submicron marine organ carbon $\delta^{13}\text{C}$ ranged from -30.4 to -27.6‰ , slightly lighter than previously published results. This could be due to the elimination of supermicron cellular material or other biologic primary emissions from the sample. In addition to bulk samples, we used size exclusion chromatography to report $\delta^{13}\text{C}$ of organic aerosols as a function of hydrodynamic volume. These results are used to infer possible origins for organic aerosols, with an emphasis on the HULIS fraction.

SOURCES OF FINE PARTICLE ORGANIC CARBON IN HELSINKI URBAN AIR

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Urban aerosol is a complex mixture of primary particulate emissions (from industry, transportation, power generation and natural sources) and secondary material formed by gas-to-particle conversion. It contains a substantial amount of carbonaceous material which is composed of elemental carbon (EC) and organic carbon (OC). EC is a primary pollutant formed in combustion processes whereas OC is a complex mixture of different groups of compounds originating from a large variety of sources. In this study the sources of OC were investigated in Helsinki using the data from the year-round measurements carried out using both on-line instruments and filter/impactor measurements.

The measurements were conducted in Helsinki (Finland) at an urban background station (SMEAR III, 60°20'N, 24°97'E, 26 m above sea level). The measurement site is located in the university campus area, 4 km northeast from the Helsinki city center. There is a densely trafficked major road (60 000 cars/day) at a distance of less than 200 m from the station. Chemical components measured on-line included OC, EC, black carbon, water-soluble ions and PM_{2.5}. Additionally, OC, EC, water-soluble organic carbon (WSOC), levoglucosan and major ions were determined from the PM₁ filter samples.

OC concentration ranged from 0.3 to 16 $\mu\text{g m}^{-3}$ from February 2006 to February 2007 with an annual mean value of 2.5 $\mu\text{g m}^{-3}$. No clear seasonal variation was found for OC. The highest OC concentrations were measured during the episodes of smokes emitted from the wildfires in Russia. The sources of OC were investigated by using a Positive Matrix Factorization (PMF) method for the PM₁ filter data. Best PMF fit was obtained for four factors which were identified as traffic, biomass combustion, secondary organic aerosol (SOA) and long-range transport (LRT). In summer the largest fraction of OC was related to SOA whereas in winter biomass combustion was the major source of OC. For LRT and traffic the seasonal variation was less pronounced.

The diurnal variation of OC was studied using the semicontinuous OC/EC analyzer. In general the diurnal variation was found to be small, however, in winter the OC concentration frequently increased in the evening, probably caused by residential heating by wood. In summer the OC concentration was slightly lower in the afternoon and in the evening than in other times of the day. That might be due to the more efficient mixing of afternoon pollutants as well as to the transfer of semivolatile OC from particle-phase to gas-phase with increasing temperature in daytime. The SOA formation was not found from the semicontinuous OC/EC data. By comparing the ambient OC/EC ratio with that obtained for traffic by PMF the contribution of traffic to OC was estimated on 3-hour basis. The contribution of traffic was at its highest from 6 AM to 9 AM being equal to 57%.

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Water-Soluble Organic Compounds in Mid-Tropospheric Aerosols

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Polar organic chemical characterization results of atmospheric aerosol (PM_{2.5}) water extracts collected at Storm Peak Laboratory (SPL) are presented. SPL is operated by the Desert Research Institute (DRI) and is located on west summit of Mt. Werner (3210m M.S.L.), near Steamboat Springs, Colorado (40.45 deg N, 106.73 deg W). The unique geographical character of SPL allows extended observations/sampling of the free troposphere. Diurnal ambient air samples were drawn through a cyclone separator (<2.5microns), followed by a 90mm TIGF filter/XAD resin sample collection cartridge to capture gas- and particle-phase analytes. Under variable meteorological conditions on January 9th through 14th 2007, the most abundant compounds were levoglucosan (9-72 ng/m³), palmitic acid (10-40 ng/m³) and succinic acid (18-27 ng/m³). The GC-MS method included a total of 84 analytes. Over 50 individual water extractable polar organic compounds were present at concentrations >0.1 ng/m³. Total daytime PM_{2.5} mass concentrations were consistently higher than night, with averages of 8.6 (+/-2.9) µg/m³ and 6.3 (+/-3.5) µg/m³, respectively. This may be due to the increased daytime convective mixing of local primary emissions from the Yampa Valley.

During a snow event (Jan. 11-13), the concentrations of several dicarboxylic acids, which may be considered as atmospheric transformation products, were reduced. Lower actinic flux, reduced transport distance, and ice crystal scavenging may explain this variability. Diurnal averages over the sampling period revealed a higher total concentration of polar compounds at night (237 ng/m³ ; 105-343 ng/m³) versus day (164 ng/m³ ; 137-205 ng/m³), which suggests a more aged nighttime aerosol character. The impact of regional and long-range transport of chemical constituents at SPL is apparent, and is most likely due to the remote/elevated geographical character. XAD resin extracts revealed a gas-phase partitioning of several compounds. A nighttime average total filter (particle-phase) and XAD (gas-phase) concentration of 197 ng/m³ (90-256 ng/m³) and 40 ng/m³ (15-87 ng/m³), respectively, confirms the particle dominated partitioning equilibrium expected for many of these compounds in the ambient atmosphere. Daytime results display a similar partitioning with a slightly lower particle/gas-phase ratio (4.667 versus 4.925), which may be due to the generally higher temperatures during the day. Variations in meteorological parameters and local/regional transport analysis play an important interpretive role in understanding these results.

Keywords: Polar Organic Compounds, Water-Soluble Organic Compounds, Aerosol Composition, Storm Peak Laboratory, Atmospheric Transformation Products.

AEROSOL CARBONACEOUS SPECIES CHARACTERIZATION IN THE SOUTH OF IBERIAN PENINSULA

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A carbon speciation study has been performed in PM₁₀ and PM_{2.5} samples collected at four sites during June 2005 to June 2006 in the Region of Andalucía, South of Spain. The sampling sites were Bailén (industrial), University Campus and La Linea (urban background), and El Arenosillo (rural) monitoring stations. Daily samples were analyzed for organic carbon (OC) and elemental carbon (EC) content by using a thermo-optical transmittance method.

Concentrations of carbon are within the range estimated by other authors for urban stations in Europe (Querol et al., 2004). Organic matter appears one of the major components of PM₁₀ and PM_{2.5} at all sites. Black carbon contributes 3–7% to PM_{2.5} and somewhat less to PM₁₀ at all sites.

A study of seasonal distribution patterns of OC and EC levels for PM₁₀ and PM_{2.5} in industrial, urban background and rural stations have been performed. OC and EC concentrations in PM₁₀ and PM_{2.5} increment from the warm to cold period in all sites, except in La Linea station where do not is show seasonal patterns for both (OC and EC), with a zig-zag pattern distributed throughout the study period. This is probably related to meteorological scenarios where the wind direction of East and West favour the dispersion of particulate matter.

The results show a gradient in organic and elemental carbon and a clear greatest contribution of both carbon species in the fine fraction (PM_{2.5}) for all sites from industrial to rural monitoring stations.

Minimum OC/EC ratios have been calculated to PM₁₀ and PM_{2.5}. The OC/EC minimum is higher in rural station (2.7-2.4) and lower in industrial (0.6-0.4) monitoring stations. Medium values ratios was obtained in both urban background stations in PM₁₀ (1.5-1.4) and PM_{2.5} (1.4-1.2). These values suggest a similar origin of organic carbon particles and similar proportions of primary organic carbon.

The minimum OC/EC ratio in rural area is similar to obtained value during periods with strong pollution from wood burning in Portugal (2.6, Castro et al., 1999). On the other hand, the OC/EC ratio in urban areas are higher than the obtained in other urban OC/EC ratios of Europe (1.1, Castro et al., 1999; 1.0, Harrison et al., 2006; Harrison and Yin, 2008).

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CHEMICAL CHARACTERISATION OF WOOD SMOKE PARTICLE EMISSIONS AND ITS APPLICATION TO SOURCE APPORTIONMENT

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Wood smoke is increasingly being seen as an important component of airborne particulate matter (PM). Recent source apportionment studies in Austria (AQUELLA) and Europe (CARBOSOL) showed that wood smoke is the main primary particle source during the winter half year (Puxbaum et al., 2007). Emissions of this source are dominated by organic and elemental carbon, together constituting around 70% of total particle emissions. Therefore it is obvious that wood combustion is one of the major primary sources of carbonaceous particles in the atmosphere as well. The source apportionment studies mentioned above applied a macrotracer concept using levoglucosan as single tracer for wood combustion (Simoneit et al., 1999). Additionally the Austrian ambient dataset was analysed with a CMB model approach to evaluate the macrotracer results. However experience with CMB showed problems with micro components, i.e. organic micro tracers, probably due to low concentrations and partly limited stability in the atmosphere and resulting difficulties in analysis.

To make use of the advantages of macrotracer and CMB model we developed a combination of the two approaches. The number of species was reduced so that we are running the CMB model on a number of 14 macro-compounds omitting organic micro tracers. This gave good correlations for most compounds except potassium where the measured values were consistently around one order of magnitude higher than the calculated (see marking in figure 1a).

To improve source profiles we investigated a number of wood combustions facilities – reaching from small-scale stoves in the power range of some kilowatts (kW) to mid-scale boilers (50kW) – regarding to their particle emissions. From the obtained dataset source profiles for different wood and application types were developed and analysed with respect to differences and similarities. Results showed that the differences in emission profiles within the group of manually fired small scale combustion units are rendered insignificant mainly due to the high variability of the combustion process, which is in good agreement with previous studies (e.g. Schmidl et al., 2008). Therefore it was decided to use one source profile for this group. Combustion conditions in automatically fired systems, however, are pretty stable after a short start-up phase and therefore also emissions are more constant. As the efficiency of combustion is much higher, the chemical composition of emissions differs significantly to manually fired appliances. Emissions from wood stoves are dominated by carbonaceous fractions (total carbon ~ 70%) while wood boilers mainly emit inorganic material (sum of ions ~ 60%).

We therefore decided to use two different wood combustion profiles in CMB modelling, one for small scale manually fired *wood stoves*, and the other for automatically fired systems (*wood boilers*). The enhanced model gave similar results for most compounds and a much better fit for potassium which can be explained by the high emission concentration of potassium in the new source profile (see figure 1b). Wood smoke source profiles and results from CMB-based source apportionment for Austrian PM10 data are presented.

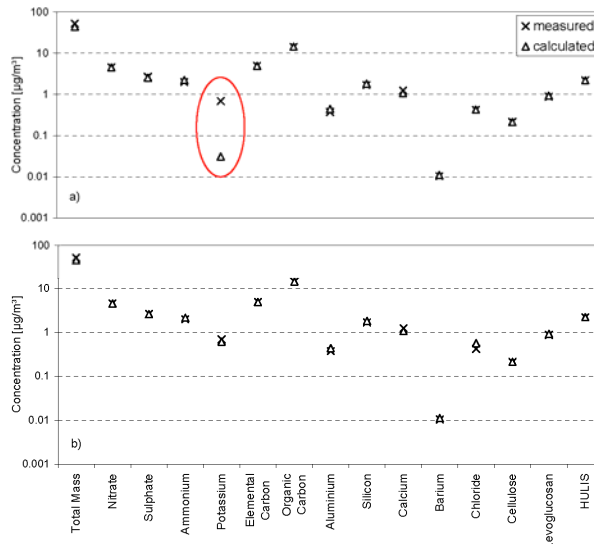


Figure 1: Measured/Calculated comparison (CMB); Original model result (a); including *wood boiler* profile (b).

**A BIOGENIC MARINE SOURCE OF ORGANIC AEROSOLS:
FROM FIELD MEASUREMENTS IN THE AUSTRAL OCEAN
TO MODEL ESTIMATES OF ITS CONTRIBUTION AT A GLOBAL SCALE**

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A continuous record of the chemical composition of bulk aerosols is performed since 2003 at the WMO-GAW global station of Amsterdam Island in the Indian sector of the Austral Ocean. Weekly filter samples collected at this station are analysed for their chemical composition (PM, ions, OC, EC, WSOC) and show a clear seasonal cycle of water insoluble organic carbon (WIOC) concentrations, with monthly concentrations of 200ngC/m³ during the Austral summer and of the order of 50ngC/m³ the rest of the year. This seasonal variation is consistent with a biogenic marine source for organic aerosols (essentially of primary origin) and extends to the Austral Ocean similar findings reported for the Northern Atlantic Ocean (*O'dowd et al.*, Nature, 2004). Further size-resolved chemical information available since 2006 at Amsterdam Island clearly shows that most of this marine organic aerosol is located in the submicron range, suggesting a significant role as Cloud Condensation Nuclei (CCN).

Despite the potential of this oceanic organic source, the global oceanic OC source is poorly quantified and not included in any global model of climate or atmospheric composition. For instance, during periods of high biological marine productivity the GEOS-CHEM global chemical transport model (CTM) underpredicts monthly-mean OC levels at oceanic surface sites (Amsterdam Island, Azores and Mace Head) by a factor of 5-20. The same CTM reproduces observed concentrations of elemental carbon (EC), sulfate and methane sulfonic acid (MSA). At Mace Head and Amsterdam Island, observed OC correlates well ($r^2 = 0.61-0.77$) with back-trajectory weighted oceanic chlorophyll-a, suggesting an OC source driven by biological activity. Using a combination of remote sensed chlorophyll-a, back trajectories and observed OC time series, an empirical relation was derived between chlorophyll-a and the primary OC emission flux. A global oceanic OC emission of 8 Tg / year was required to match observations (NMB 7%), and results in 20% increase in the global atmospheric OC burden. This emission represents a significant flux of OC to the global atmosphere which is missing from models, comparable in magnitude to the fossil fuel OC source (*Spracklen et al.*, Geophys. Res. Lett., in press).

WATER-SOLUBILITY AND VOLATILITY OF FRESH SECONDARY ORGANIC AEROSOLS

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Secondary organic aerosols (SOA), which represent a large - if not major - fraction of fine airborne particles, are expected to induce significant effects on local to global climate. In particular, they could act as cloud condensation nuclei (CCN) and are then considered as possible key contributors to the aerosol indirect effect and to the alteration of the water cycle. Therefore, a particular attention has been recently paid to SOA and to their water-solubility. Results obtained so far seem to indicate that SOA formed in anthropogenic-influenced air masses may be composed almost exclusively of water-soluble species. Such findings notably suggest that urban SOA concentrations may be adequately approximate by water-soluble organics. However, SOA formation/transformation mechanisms are still poorly understood, and it is not clear yet if such results may be extrapolated to every urban atmosphere. In this study, diurnal variations of carbonaceous aerosols were investigated in two contrasted megacities: Paris (France) and Cairo (Egypt). Results presented here indicate significant formation of both water-soluble and water-insoluble SOA during afternoon in these two urban centres. Moreover, a large fraction of these fresh SOA seems to be present in the form of semi-volatile organic matter (SVOM). These findings are discussed in light of meteorological conditions and of gaseous precursor origins (anthropogenic vs. biogenic).

Factors influencing urban carbonaceous aerosols: comparison of Beijing (RP China), Paris (France), Cairo (Egypt) and Ouagadougou (Burkina Fasso)

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Fine and coarse aerosols were sampled in various urban environments. Following a chemical mass balance methodology **, it could be possible to achieve their chemical closure and to scrutinize the seasonal variations of source fingerprints and aerosol transformations. Results for annual sets of weekly samples obtained and analyzed same way in three very different megacities (Beijing, Paris, Cairo) and Ouagadougou the capital of Burkina Faso, are presented in this talk.

For all cities and for somewhat different reasons, carbonaceous particles form the major and often overwhelming fraction of the fine aerosols. Chemical composition is thus discussed in light of prevailing sources, meteorological conditions (temperature, humidity, wind sector) and gas-to particle interactions.

Interestingly, carbonaceous particles are also found in the coarse aerosol fractions, presumably as both primary and secondary particles. The latter are assessed to originate primarily from gas-particle interactions of acidic organic gases with dust particles, creating a significant anthropogenic fraction in the coarse mode.

Both fine and coarse particles show variable amounts of water soluble organic carbon (WSOC) which is shown to depend on different factors such as the source type, the importance of secondary aerosol formation and the aerosol matrix.

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SPATIAL AND TEMPORAL VARIATIONS OF AEROSOL OPTICAL AND CHEMICAL PROPERTIES AT FIVE CANADIAN SITES

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Aerosol optical properties are related to its various chemical components; black carbon absorbs radiation while sulfate and organic carbon are efficient light scatterers. Spatial and temporal variations of the optical and chemical properties are presented at five different sites across Canada for 2005-2007: (1) Alert, Nunavut at the northern tip of Ellesmere Island in the high Arctic; (2) BERMSTT, Saskatchewan in the southern edge of the Canadian boreal forest; (3) Fraserdale, a forested site in Ontario and located in the southern perimeter of the Hudson Bay Lowlands; (4) Egbert, Ontario in the rural region located about 80 km north of Toronto; and (5) Whistler, British Columbia at the altitude of 2,180 m MSL in the Pacific Ranges of the Coast Mountains. Each site is unique as it is impacted by emissions from regional sources, which are superimposed on continental background aerosols. The atmosphere at Alert is characterized by the winter/spring accumulation period of the “Arctic Haze”. BERMSTT regularly experiences impact of biogenic aerosols and smoke plumes from summertime boreal forest fires. Fraserdale is often impacted by forest fires and biogenic with occasional anthropogenic influence. Egbert experiences relatively clean air mass when winds come from the north and northwest, whereas winds from the south and southwest typically carry various anthropogenic aerosols to the site. Finally, Whistler was selected as a site to study changes in the free tropospheric aerosol, as well as to monitor changes in the intercontinental transport of Asian aerosols across the Pacific. This site also experiences a strong biogenic influence in the spring and summer. The median (mean) aerosol light extinction are 6.2 (7.3) Mm^{-1} at Alert, 7.1 (10.4) Mm^{-1} at Whistler, 7.1 (15.4) Mm^{-1} at BERMSTT, 7.5 (14.2) Mm^{-1} at Fraserdale and 8.5 (17.7) Mm^{-1} at Egbert, respectively. Mass scattering efficiencies will also be presented by looking at the relationships between the aerosol light scattering and sulfate and organic carbon mass concentrations at all sites.

SECONDARY ORGANIC PARTICLE FORMATION FROM REACTIONS OF AMINES WITH NITRATE RADICAL

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Alkyl amines are a class of volatile organic compounds emitted in large quantities from animal husbandry and concentrated animal feeding operations. Reports in the literature have indicated the presence of amines in the particulate phase for several decades. However a comprehensive study of their particle formation potential has not been reported previously. Recent work in our laboratory shows that in ambient fine particulate matter, amine-related compounds exhibit a strong diurnal pattern, peaking at nocturnal hours. To examine the potential for nighttime reactions of amines to lead to secondary organic aerosol formation, we have investigated reactions of amines with nitrate radical using an aerosol mass spectrometer and a proton transfer reaction mass spectrometer.

Three tertiary amines were studied; trimethylamine, triethylamine, and tributylamine. Results indicate that tributylamine forms the largest amount of fine particulate mass followed by trimethylamine and triethylamine respectively. Particle formation from these reactions is very high compared to most other atmospheric reactions of volatile organic compounds; *e.g.* the yield ($M/\Delta M$) for the reaction between trimethylamine and nitrate radical is 65%. Mass spectra from the aerosol mass spectrometer point to complex non-salt aerosol products. One component identified in the products is the presence of di-hydroxy amides. For tertiary amines, we propose a mechanism that proceeds via abstraction of a proton by the nitrate radical followed by RO_2 chemistry. Rearrangement of the alkoxy radical through H-shift leads to the formation of aerosol products.

The reactions of primary and secondary amines with nitrate radical also result in significant particulate products. Indeed several primary amines show even higher rates of conversion into the particulate phase than the tertiary amines, though the products and particulate formation mechanisms appear different than for the tertiary amines. Primary amines react to form secondary carbonaceous aerosol through an imine precursor while secondary amines appear to engage dominantly in acid-base chemistry with nitric acid.

These experiments show that night-time oxidation of amines by nitrate radical can be an important source of secondary carbon particles in regions with high mixing ratios of these species. This work also shows the importance of understanding contributions of agricultural emissions as a secondary source of carbonaceous particulate matter, an area that has been overlooked in both regional and global chemistry models of particles.

OH Oxidation of Organic Aerosols

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Heightened concern over global climate change has led to increased scrutiny of the direct and indirect effects of aerosols on radiative forcing, and particle size and chemical composition are important factors in determining the magnitude of such effects (1). Heterogeneous reactions of organic aerosols (OA) with gas-phase oxidants can alter both composition and size, in some cases activating the particles for cloud formation (2). Furthermore, as a result of volatilization of OA oxidative aging may also liberate a host of volatile organic compounds (VOCs) that are potentially important intermediates in photochemical cycles such as smog formation (3). Here we present results from recent experiments on oxidative ageing of OA with OH radicals using a photoionization aerosol mass spectrometry experimental setup at the ALS/LBNL. We have determined that OH reactions with simple particle phase alkanes, such as squalane (Sq) proceed by a sequential oxidation mechanism. Depending on OH concentration and exposure time, these simple oxidation products, i.e. SqO, SqO₂, SqO₃, etc (products consisting Sq hydrocarbon chain with progressively added oxygen atoms) account for 50-80% of the particle by mass. The formation mechanisms of these particular products can be well understood by the analogous gas phase reactions between OH and small alkanes. However, the remaining 20-50% of the particle phase appear to be transformed into high molecular weight compounds ($500 > m/z < 1000$). Currently, there are no known analogous gas phase reactions that could account for the production of these complex species. Understanding the chemical origin and formation mechanisms of these high molecular weight compounds within the aerosol phase is particularly important since similar oligomeric material has been found to be a major component of ambient organic aerosol and might account for as much as 50% of the aerosol mass. (4). In addition to these mechanistic details we have also employed a relative rates technique in order to determine the heterogeneous reaction rates of OH with OA. We have found that the reaction is first order over a large range of OH concentrations, and the uptake coefficient is near unity.

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CHEMICAL CHARACTERIZATION OF HUMIC LIKE SUBSTANCES (HULIS) IN NORTH AMERICAN ATMOSPHERIC AEROSOLS USING LC-MS/MS

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Several studies have suggested that humic-like substances (HULIS) in atmospheric aerosols make up an important fraction of ambient organic aerosol mass, and may play an important role in cloud processing. HULIS is operationally defined as water-soluble, polyacidic, refractory, high-molecular weight organic material that has similar characteristics to aquatic humic and fulvic acids. The chemical origin of HULIS is poorly understood, and may originate from secondary organic aerosol formation, biomass burning, and/or other sources. In this study, we used liquid chromatography, triple-quadrupole mass spectrometry (LC-MS/MS) to investigate chemical and structural characteristics of HULIS in atmospheric aerosol samples from several locations in North America. These sites were chosen to reflect contrasts in known aerosol sourcing. Water-soluble components of ambient aerosol were separated using hydrophilic interaction liquid chromatography (HILIC). Tandem mass spectrometry provided two fragmentation and separation steps. The first separation selected mass fragments in the molecular weight range of 200-600 amu and the second step focused on specific fragments related to chemical structure. Fragments indicative of carboxylic acids, aromatic carboxylic acids, aliphatic carboxylic acids, carbohydrates, and sulfate esters were identified. Surrogate compounds were used to confirm fragmentation pathways and to aid in quantification. The chemical composition of HULIS from Atlanta, Georgia; Riverside, California; Fresno, California; Bondville, Illinois; and two locations in Mexico City, Mexico was characterized. The atmospheric HULIS structures were systematically compared to standardized aquatic humic and fulvic acids from the Suwannee River, Georgia. The selected sites of atmospheric aerosol collection had well-studied primary sources and important contributions from secondary aerosol sources. This knowledge provided a basis for understanding structural characteristics of HULIS in the context of both primary and secondary aerosol sources.

SOURCE APPORTIONMENT OF CARBONACEOUS AEROSOL IN THE KATHMANDU VALLEY: SENSITIVITY TO BIOMASS SOURCE PROFILES

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Daily samples of fine particulate matter were collected at Godavari, Nepal in the Kathmandu Valley throughout the year of 2006. The annual trend in ambient concentrations of particulate mass, elemental carbon (EC), and organic carbon (OC) indicate maximum concentrations occurred during the dry season and minimum concentrations occurred during the monsoon season. Specific organic compounds unique to aerosol sources—molecular markers—were measured by month and were used to identify the following aerosol sources: motor vehicles, coal combustion, biomass combustion, vegetative detritus, and secondary organic aerosol. A molecular marker-based chemical mass balance model was used to provide a quantitative assessment of primary source contributions to ambient carbonaceous aerosol. Biomass combustion and motor vehicles were both major sources of EC. The majority of OC was unapportioned to primary sources and was attributed to secondary organic aerosol formation.

This study focuses on better understanding the chemical distinction between biomass burning at different burn rates. A previous study has shown that biomass burning at low rates produces significantly more elemental than organic carbon ($EC/OC > 1$) compared to burning at high rates ($EC/OC < 1$). Biomass burning at low rates is believed to be important in the south Asian region due to combustion conditions of residential stoves used for heating and cooking. Molecular marker-based source profiles for four types of wood, burned at both high and low rates, are presented for the first time. The sensitivity of source apportionment to biomass profiles was studied using these new profiles and others drawn from the scientific literature. This study concludes that the selection of source profiles has only a minor impact on apportionment of organic carbon, but has a major impact on the apportionment of elemental carbon.

TOWARDS A REFERENCE MATERIAL FOR SOOT MEASUREMENT: EVALUATION OF CANDIDATES WITH SCANNING ELECTRON MICROSCOPY, AN SP2, A PASS AND AN OC/EC ANALYZER

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Atmospheric strongly-light absorbing carbon (LAC) detected with thermal and thermal/optical analysis techniques is called elemental carbon (EC), while LAC measured with optical instruments is called black carbon (BC). There can be considerable variation between EC or BC measured by different instruments due to analytical differences and interferences by other materials like organic carbon. This is accentuated by the lack of a reference material for LAC that can be used to calibrate different measurement techniques to the same standard. Depending on the measurement technique, a reference material should have some or all of the following: an established composition and density, reproducible and adjustable size distribution, and known optical properties. The reference material should also be stable over extended periods of time.

We examined a number of reference material candidates using a DMT single particle soot photometer (SP2), a DMT photoacoustic soot spectrometer (PASS), a Sunset Labs thermal-optical analyzer and electron microscopy. Both Alfa Aesar[®] and Tokai[®] glassy carbon have the advantage of a spherical shape and known density. Fullerene soot has a fractal shape like combustion soot and a low density, which is useful when calibrating instruments at BC masses of 1 fg or lower. Acheson AquaDAG[®] shows well-defined, narrow peaks through a DMA, but the density of the particles is not known even to the manufacturer.

In the SP2, the ratio of incandescent signals collected over two different wavelength bands produces a signature that is characteristic of the incandescent material (1). In addition to LAC, certain metals also incandesce. However, our studies show that atmospherically-common metals like silicon and chromium have a signature distinct from the diffusion flame-generated soot of Kirchstetter and Novakov (2). More encouragingly, glassy carbon, fullerene soot and AquaDAG all show a signature consistent with that of the flame-generated soot.

Graphitized thermal soot (GTS), produced at Moscow State University, has an EC content over 99.9% when analyzed with an OC/EC analyzer. TEM has shown that GTS has a spheroidal shape (3), which helps ensure that DMA size segregation produces particles of known size. Results from pure and coated GTS tests with the SP2 and PASS will also be reported.

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ORGANOSULFATE FORMATION IN BIOGENIC SECONDARY ORGANIC AEROSOL

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Enhancements in laboratory-generated secondary organic aerosol (SOA) from several biogenic volatile organic compounds, including isoprene and monoterpenes, have recently been observed when increasing the acidity of preexisting sulfate seed aerosol. Acid-catalyzed particle-phase reactions, some of which lead to the formation of high molecular weight species through oligomerization, have been proposed to explain these observed enhancements. The importance of acid-catalyzed particle-phase reactions to ambient aerosol remains highly uncertain, as currently there is no chemical evidence for their respective products, and with the exception of esterification of organic compounds, most of these reactions are not thermodynamically favorable under ambient conditions.

Organosulfates of isoprene, α -pinene, and β -pinene have recently been identified in both laboratory-generated and ambient SOA. In this study, the mechanism and ubiquity of organosulfate formation in biogenic SOA is investigated by a comprehensive series of laboratory photooxidation (i.e. OH-initiated oxidation) and nighttime-oxidation (i.e. NO_3 -initiated oxidation under dark conditions) experiments using nine monoterpenes (α -pinene, β -pinene, *d*-limonene, *l*-limonene, α -terpinene, γ -terpinene, terpinolene, Δ^3 -carene, and β -phellandrene) and three monoterpenes (α -pinene, *d*-limonene, and *l*-limonene), respectively. Organosulfates were analyzed and characterized using liquid chromatographic techniques coupled to electrospray ionization combined with both linear ion trap and high-resolution time-of-flight mass spectrometry. Organosulfates are formed only when monoterpenes are oxidized in the presence of acidified sulfate seed aerosol, a result consistent with prior work. Archived laboratory-generated isoprene SOA and ambient filter samples collected from the southeastern U.S. were reexamined for organosulfates. By comparing the tandem mass spectrometric and accurate mass measurements collected for both the laboratory-generated and ambient aerosol, previously uncharacterized ambient organic aerosol components are found to be organosulfates of isoprene, α -, β -pinene, and limonene-like monoterpenes (e.g. myrcene), demonstrating the ubiquity of organosulfate formation in ambient SOA. Several of the organosulfates of isoprene and of the monoterpenes characterized in this study are ambient tracer compounds for the occurrence of biogenic SOA formation under acidic conditions. Furthermore, the nighttime-oxidation experiments conducted under highly acidic conditions reveal a viable mechanism for the formation of previously identified nitrooxy organosulfates found in ambient nighttime aerosol samples. We estimate that the organosulfate contribution to the total organic mass fraction of ambient aerosol collected from K-pusztá, Hungary, a field site with a similar organosulfate composition as that found in the present study for the southeastern U.S. fine aerosol, during the 2003 summer campaign can be as high as 30%. Based upon the potential significance of this estimate (and other recent estimates), it is essential that the detailed chemical characterization of organosulfates be conducted, as done in the present study, since this will lead to improved understanding of their formation pathways in ambient organic aerosol.

REFINED ^{14}C SOURCE APPORTIONMENT OF ORGANIC CARBON

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Carbonaceous particles originate from different anthropogenic and biogenic sources. Major anthropogenic emissions result from fossil-fuel combustion and biomass burning. Biogenic carbonaceous aerosols mainly comprise plant debris, pollen, fungal spores, and bacteria as primary particles and secondary organic aerosol (SOA) from biogenic gaseous precursors. For the identification and quantification of these sources, radiocarbon (^{14}C) determinations offer a unique possibility for unambiguous source apportionment of carbonaceous aerosol particles. Because ^{14}C has decayed in fossil material, this isotopic method enables a direct distinction of fossil and non-fossil carbon in ambient aerosols, which has been applied to organic carbon (OC) and elemental carbon (EC) (Szidat et al., 2006).

We present a refinement of this source apportionment strategy by direct ^{14}C measurement of several sub-fractions of OC: a) Water-soluble OC (WSOC), which could only be estimated indirectly from the measurement of water-insoluble OC before (Szidat et al., 2004); b) the fraction of humic-like substances (HULIS), which is isolated using the method of Limbeck et al., 2005; c) simple dicarboxylic acids like oxalic acid separated with HPLC. We show results from ambient aerosols collected during a summer campaign at rural site in the Po valley, northern Italy, and discuss the importance of fossil and non-fossil SOA.

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USING HOURLY OC/EC RATIOS FOR ESTIMATING SECONDARY ORGANIC AEROSOL LEVELS: PROGRESS AND PERILS

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Carbonaceous aerosols—elemental carbon and a diverse mixture of organics—constitute a major portion of $PM_{2.5}$ mass in the ambient atmosphere. Effective control strategies for this fine mass component will likely involve both reductions in primary emissions as well as emissions precursors of secondary organic aerosols (SOA). Approaches to source allocation of SOA have included: a. measuring total organic aerosol carbon and the tracers of specific sources of primary organic carbon, then using CMB, PMF, or equivalent modeling approaches to apportion sources of primary OC mass, assuming that un-apportioned organic mass is SOA; b. measuring surrogates for SOA or some SOA products formed from specific precursors, for example, measuring water-soluble OC mass and assuming that it is all SOA; c. estimating OC/EC ratios from emissions inventories of OC and EC specific sites, or calculating ratios for samples in assumed to contain negligible amounts of secondary aerosol (formed during transport). Changes in ratios (increases from primary only values) are used to estimate what fraction of the observed OC mass is secondary under other conditions, assuming the primary OC/EC ratio remains constant.

In this work, we have examined the applicability of the primary OC/EC ratio method for the estimation of SOA levels at three locations in the Tennessee Valley region—an urban site with significant industrial emissions (Chattanooga, TN), a small urban/suburban location (the Shoals, in NW Alabama), and a rural site (Look Rock, TN) not close to significant emission sources. Blank-corrected hourly data for OC and EC were used for analyses at the urban/suburban sites (Sunset Labs instrument), and a combination of hourly TC (R&P instrument) and Aethalometer black carbon (BC) data were used in the rural site, with OC calculated as $TC - BC$ in the latter case. Specific periods with apparently minimal SOA levels, as indicated by values for several species ($PM_{2.5}$, SO_4^{2-} , TC), were examined to estimate SOA and its uncertainty at these sites, using previous approaches (Turpin and Huntzicker, 1995, Strader et al., 1999; Polidori et al, 2006). Seasonal differences in the magnitude of calculated SOA, and in the minimum OC/EC ratios used to estimate it at the urban/suburban and rural sites were also examined. Estimates were made of the reliability with which the primary OC/EC ratio used in calculating SOA could be estimated at various types of sampling sites, depending on the magnitude of precursor emissions and the distance between sources and the sampling site.

Data for Chattanooga for June, 2005, indicate that a relatively robust estimate of the minimum OC/EC ratio (3.0 ± 0.2) could be made under 'clean' conditions which was then used to generate estimated SOA (range: $0-8 \mu g/m^3$) under late spring-early summer conditions. Data from one-month periods at the Shoals location in various seasons indicated that wintertime minimum OC/EC ratios during periods of low sulfate and $PM_{2.5}$ mass were stable (about 3.3 ± 0.3), with calculated SOA in the $0-0.8 \mu g/m^3$, and consistent with reported winter data at this site (Ke et al., 2007), but were higher and less stable in spring and summer conditions. Difficulties in using this approach at Look Rock will be discussed in detail. Diurnal patterns of estimated SOA show seasonal variations consistent with gas-to-particle SOA formation in summer and contemporary carbon combustion in winter.

CALIBRATION OF PHOTOACOUSTIC AEROSOL ABSORPTION MEASUREMENTS WITH OXYGEN A-BAND SPECTROSCOPY

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Photoacoustic Measurements can be used as first-principle determination of light absorption. Calibration can be achieved using gaseous light absorption of a gas with well-known absorption coefficient at the operating wavelength of the photoacoustic instrument. An obvious choice is the absorption of the oxygen (O₂) A-band in the 760-770 nm spectral region, where external-cavity diode lasers with sufficient output power are readily available. We discuss first results on the simultaneous measurement of oxygen A-band absorption with wavelength and power modulated photoacoustic spectroscopy and aerosol absorption with power modulated photoacoustic spectroscopy.

INFLUENCE OF ENVIRONMENTAL CONDITIONS ON CARBONACEOUS PARTICLE CONCENTRATIONS WITHIN NEW ZEALAND

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Carbonaceous particulate matter in our environment is primarily anthropogenic in origin. The concentrations of particulate matter observed within several New Zealand airsheds are only sometimes correlated with the population and/or source activity within the respective airsheds. Source apportionment studies from several locations around New Zealand (including Auckland, Hastings, Wairarapa, Hutt Valley, and Christchurch) have helped to identify black carbon (BC) particulate sources which are often the major component of ambient air particulate matter (APM), especially in winter. Black carbon has been found to originate primarily from traffic and domestic home heating. While particulate matter from traffic sources can have elevated concentrations for short durations during peak traffic flows, the average traffic particulate concentration correlates with the population living within an airshed. Conversely, the contribution of particulate matter from domestic home heating to APM is observed to be independent of the airshed population. This is because particulate matter from domestic home heating often builds up during cold calm nights with the presence of inversion layers which significantly limits vertical dispersion of the APM and thus confining the BC air particulate matter to a limited atmospheric volume. Hence the average winter home heating particulate concentration within the airsheds studied is attributed more to environmental confinement rather than source production.

Key Words: Carbonaceous particulate, Source Apportionment, Source activity, Meteorology, Environmental conditions, New Zealand.

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CARBONACEOUS AEROSOL: PHYSICAL NANOSTRUCTURE AND CHEMICAL ANALYSIS BY XPS

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Epidemiological studies have shown that inhalation of soot particles can cause pulmonary disease, cardiovascular damage and mortality. New findings show soot may be contributing to changes happening near the North Pole, such as accelerating melting of sea ice and snow and changing atmospheric temperatures. Soot surface chemistry may determine whether it can act as cloud nuclei, its participation in atmospheric heterogeneous reactions, thereby significantly affecting the atmospheric radiative balance. These properties are further modified by soot's nanostructure, along with its oxidation characteristics. With increasing knowledge of the detrimental health effects of soot and environmental impacts, identification of emission sources is of increasing importance

Electron microscopic and spectroscopic methods have great potential for carbonaceous aerosol characterization. High-resolution transmission electron microscopy (HRTEM) provides information of the carbon nanostructure (or relative lack thereof). Image quantification allows extraction of various statistical parameters including lamella length, separation distance and tortuosity. These may be summarized in the form of histograms. X-ray photoelectron spectroscopy (XPS) provides a means for probing the surface chemistry of materials. It provides not only information about the atomic composition of a sample but also information about the structure and oxidation state of the constituent elements.

Combustion produced soot is a highly variable material. Physically the nanostructure can range from amorphous to graphitic to fullerenic. Chemically nearly any element could be included, though the surface functional groups are predominantly oxygen-based. Results will be presented for analysis of HRTEM images of the physical nanostructure and XPS analysis of the chemical composition of soots collected from plant, institutional and residential scale oil-fired boilers, diesel engine, gas-turbine combustor (jet) and a wildfire. Physically soots from these emission source classes may be differentiated based on carbon lamella length, mean separation and tortuosity. Chemically these soots may also be distinguished by elemental composition, surface (oxygen) functional groups and carbon bonding.

Characterization of source (particulate) emission profiles is integral to formulation of source profiles towards development of receptor-based models and extraction of source contributions to monitored sites. Atmospheric and local environmental impacts can then be accurately assessed. Regulatory statutes may be specifically targeted. Human exposure and related health effects can be accurately evaluated.

KINETIC CONTROL OF THE CLOUD PROCESSING OF METHYLGLYOXAL IN AEROSOLS: IMPLICATIONS FOR THE CLIMATE FORCING PROPERTIES OF ORGANIC AEROSOLS

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Aerosols undergo significant and rapid changes in water content and acidity during cloud formation and evaporation that can drive chemical reactions which alter the size and chemical composition of the aerosol organic fraction, thereby impacting the climate-forcing properties of the aerosols. Here we examine a model organic aerosol component, methylglyoxal, which exists in aqueous solution as a mixture of its monohydrate, its dihydrate, various polymers, and its “free” dicarbonyl form. Our NMR and UV-vis experiments demonstrate that changes in chemical speciation occur upon dilution of aqueous solutions of methylglyoxal and therefore occur in atmospheric aerosols during cloud formation. In particular, dilution drives the methylglyoxal hydration reactions as well as the decomposition of some polymers and the formation of other polymers. These chemical changes occur on timescales of hours indicating that methylglyoxal does not necessarily reach chemical equilibrium in cloud droplets before evaporation (or precipitation). This result shows that the chemical speciation of methylglyoxal (and likely other alpha-dicarbonyls) in cloud droplets is under kinetic control and that the effects of cloud-processing chemistry on aerosol climate-forcing properties therefore may not be well described by chemical equilibrium conditions.

TWO SOURCES OF UNCERTAINTIES IN MODELLING BLACK CARBON AT GLOBAL SCALE

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Black Carbon (BC) has a significant influence on both air quality and radiative forcing. The common term “black carbon” is highly ambiguous, as it has no clear definition. It is used in the emission inventories to describe emissions that may be a mixture of black carbon and elemental carbon (EC) depending on the measurements used for derivation of emission factors. Black carbon and elemental carbon are operational definitions related to absorption of light or refractory properties, respectively.

Our understanding of the global black carbon cycle is rather qualitative due to uncertainties in our knowledge of both the emissions of BC and the physical and chemical processes by which it is aged and removed from the atmosphere. This work investigates the uncertainties arising from i) choosing the way to describe BC properties in the global Chemistry-Transport Model TM5 (bulk approach, simple treatment in the removal processes versus microphysical aging within an aerosol dynamics model, with the removal dependent on the microphysical properties of the aerosol) and ii) comparing the resulting concentrations with measurements.

The comparison with the observations shows that close to the sources the two approaches do not give significantly different results, being the emissions the prevailing mechanism. In more remote areas such as oceanic and polar regions the differences are up to orders of magnitude, the more complex treatment of BC giving results closer to the measured values. Using the dynamics approach, the model estimates that globally 60% of BC mass remains interstitial when clouds are present. Assuming the same partitioning between interstitial particles and cloud condensation nuclei in the bulk approach the model results do not significantly improve in remote areas.

Unfortunately, the observations that can be used for an evaluation of a global model are sparse, and comprise both measurements of EC and BC, adding difficulty and uncertainty in the model evaluation.

MODELLING THE IMPACT OF PRIMARY INSOLUBLE ORGANICS FROM THE SEA

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The chemical composition of the marine aerosols as a function of their size is an important parameter for the evaluation of their impact on the global climate system. In the last years soluble and insoluble organic material has been found in measured marine aerosols and its potential impact has started to be the focus of modelling studies.

In this study we model the impact of the primary insoluble organic matter emitted from the sea on the chemical and physical properties of the aerosols at global scale using the Chemistry-Transport Model TM5. TM5 is an off-line global model that uses the meteorological fields calculated by the ECMWF model. It has a spatial global resolution of $6^\circ \times 4^\circ$ and a two-way zooming algorithm that allows resolving regions with a finer resolution of $1^\circ \times 1^\circ$. Surface processes are globally treated on a resolution of $1^\circ \times 1^\circ$. The coupling with the microphysical aerosol dynamics model M7 allows the resolution of particle masses and numbers in size. The mass of the emitted sea spray particles is partitioned between insoluble organic and sea salt components, using a function that relates the emitted organic fraction in sub-micron range to the surface ocean chlorophyll-a concentrations.

The modelled particulate organic matter monthly surface fields show the highest increase over the oceans compared to fields calculated without marine sources. Following the seasonality of the biological activity at the sea surface the organic mass fraction in the sea spray is higher in summer in the Northern hemisphere and in winter in Southern Hemisphere. The resulting contribution of the marine insoluble organic emissions compared to the total global particulate organic matter emissions depends on the season, being higher in winter than in summer.

The modelled fields are evaluated against water insoluble organic measurements.

CHARRING CHARACTERISTICS OF WATER-SOLUBLE ORGANIC CARBON FROM SAMPLES WITH DIESEL EXHAUST FUME AND WOOD SMOKE ANALYZED BY A THERMO-OPTICAL TRANSMITTANCE METHOD

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ABSTRACT

Carbonaceous aerosols contain a soluble part and an insoluble, refractory part. The soluble part contains substances that are soluble in either water or organic solvents. A common method to analyze carbonaceous aerosols is thermo-optical analysis (TOA) that assigns the refractory part as elemental carbon (EC). EC is therefore not “elemental” carbon as such but rather a fraction of carbon that is operationally defined by the analyzing method.

For this experiment the objective was to investigate if water soluble carbonaceous compounds could be responsible for any misclassification of EC using the NIOSH method NMAM 5040 with a Thermo-Optical Transmittance analyzer (Sunset Labs). Filter samples from eight different aerosol environments were used; from pure diesel exhaust fume with a high content of EC and also with a low content of EC, pure wood smoke, pure bio diesel exhaust fume, an urban road tunnel, an urban street canyon, an urban background site and residential wood combustion in an urban area. Each filter sample was extracted with water and this water extract was subsequently filtrated to remove all particles.

Only for three samples was EC detected in the water-soluble extract: pure wood smoke (18 % of original EC), residential wood combustion in an urban area (12 % of original EC) and urban background (7 % of original EC). The urban background sample contained long-range transported particles from agricultural fires in Eastern Europe and also possibly pollen from plants. Since no carbon-containing particles were present in the water-soluble extract, one possibility is that some refractive water-soluble light absorbing carbon species exists in the sample, either from the beginning or pyrolytically formed during the oxygen-free part of the analysis. These substances would then not combust and evolve until oxygen is introduced.

This would implicate that when measuring EC in environments with local combustion particles from wood smoke or other biomass burning, some water-soluble carbonaceous compounds (or thermally degraded compounds thereof) could also be determined as EC by the NIOSH method.

RELATING OC/EC DATA FROM TWO NATIONAL MONITORING NETWORKS

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IMPROVE (Interagency Monitoring of PROtected Visual Environments) is a particle sampling network designed to track regional haze in rural and remote locations. CSN (Chemical Speciation Network) is a particle sampling network designed to support health studies and source apportionment of urban air pollution. Both networks use thermal-optical analyses to determine “elemental” and “organic” carbon in 24-hour samples collected on quartz filters. Differences in their sampler designs, filter handling, analytical protocols and data reduction nevertheless yield significant differences in their reported concentrations. This paper examines the empirical relationships that can be observed in data from several years of collocated monitoring at 12 urban sites, and their implications for integrative data interpretation.

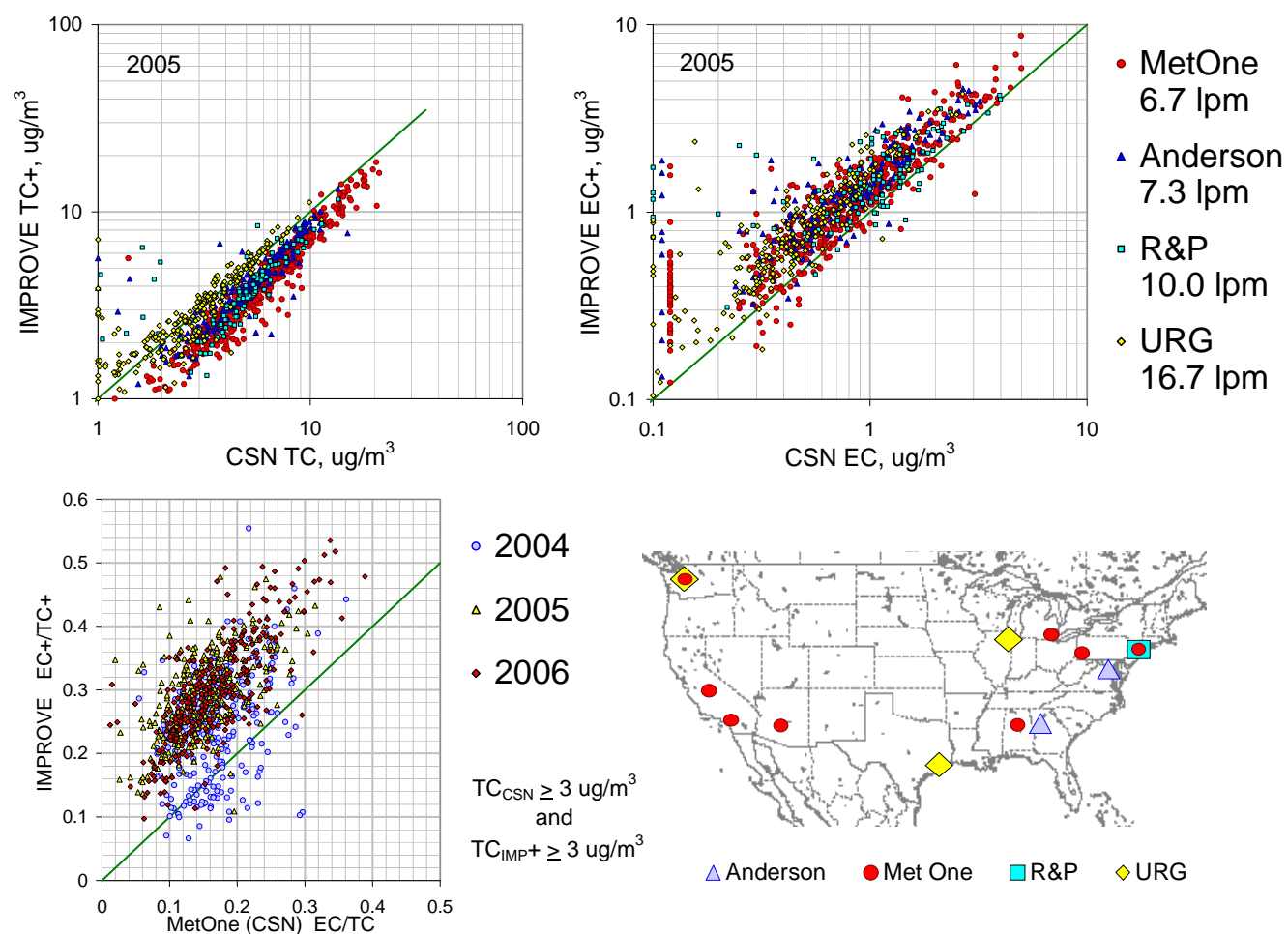


Figure: Comparisons of IMPROVE and CSN data from collocated monitoring at twelve urban locations (map, bottom right). IMPROVE generally reports more EC than CSN, and less TC than CSN (top); the differences vary with CSN sampler for TC (left), but not for EC (right). The minimum fraction of TC reported as EC by IMPROVE increased in 2005 (bottom left), when aging analytical instruments were replaced. CSN concentrations are reported with no adjustment for sampling artifacts; the “artifact corrections” that are subtracted from reported IMPROVE concentrations were accordingly added back in for these comparisons.

SIZE DISTRIBUTIONS OF HULIS IN FRESH BIOMASS BURNING AEROSOLS AND AMBIENT AEROSOLS IN SOUTH CHINA

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Humic-Like Substances (HULIS) constitute a significant fraction of water soluble organic aerosol mass and influence the water uptake properties of aerosols in the atmosphere. Burning of crop residue after harvest is common in China and represents a significant source for ambient aerosols. In this work we examine particle size distribution of HULIS in the fresh emissions of burning sugar canes and rice straws and in the ambient aerosols collected in a location in south China. HULIS is separated from other inorganic ions and low molecule weight organic compounds co-existing in aerosols using solid phase extraction and then quantified by an evaporative light scattering detector (ELSD), a quasi-universal mass detector suitable for the quantification of compounds of unknown structures and without authentic standards.

Preliminary results show that HULIS is abundant in both fresh biomass burning and atmospheric aerosols and has a dominant accumulation mode (0.18-1.8 μm) (Figure 1). The HULIS/OC ratios are nearly constant in different size bins of fresh biomass burning aerosols. It is found that the HULIS/OC values in the accumulation size bins in the ambient samples are significantly higher than those in the fresh biomass burning aerosols. Our results indicate that biomass burning is a significant source of HULIS and there are other significant sources of HULIS in the atmosphere in addition to biomass burning.

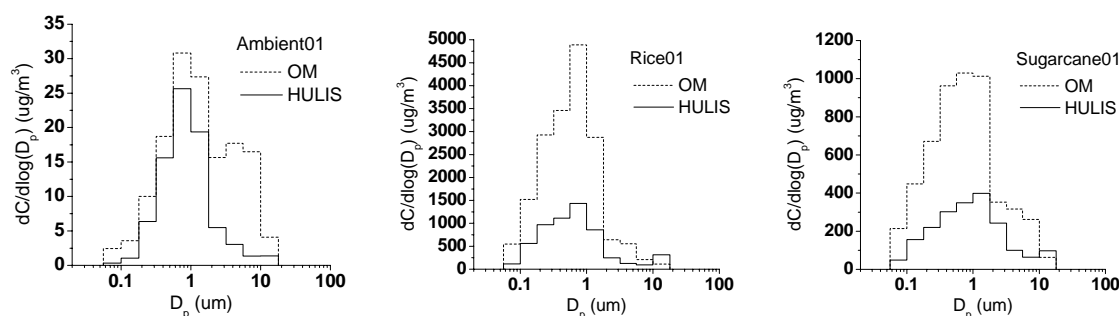


Figure 1. Particle Size distributions of HULIS in ambient samples and in particles freshly emitted from rice straw and sugarcane leaves burning in Pearl River Delta region.

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CONTRIBUTIONS OF URBAN, BIOMASS BURNING AND SECONDARY ORGANIC AEROSOLS NEAR MEXICO CITY

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Abstract

Organic aerosols (OA) within and downwind of Mexico City can be classified into three broad categories: 1) primary organic aerosols (POA) directly emitted from urban sources (e.g., vehicular exhaust), 2) biomass burning organic aerosols (BBOA) directly emitted from forest/vegetation fires, and 3) secondary organic aerosols (SOA) from gas-to-particle conversion of semi-volatile and non-volatile organic species formed as a result of photooxidation of volatile organic compounds (VOCs) of both anthropogenic and biogenic origins. It is of great interest for both air quality and climate forcing purposes to quantify the contributions of these three types to the total OA mass loading within and downwind of Mexico City. The Aerodyne Aerosol Mass Spectrometer (AMS), which was deployed at multiple ground sites as well as onboard the DOE G-1 and NSF C-130 aircraft, has been particularly useful for obtaining high time-resolution measurements of PM_{2.5} OA mass concentrations. However, the difficulty lies in determining the contributions of POA, BBOA, and SOA to the observed total OA mass.

In this paper we focus on the analysis of the 10-min average AMS and PTR-MS data at the T1 ground site (just outside of Mexico City to the north) to estimate the three OA fractions. We make use of acetylene (C₂H₂) and acetonitrile (CH₃CN) mixing ratios as tracers of urban and biomass burning emissions, respectively, to first determine the POA and BBOA masses with the rather straightforward multi-linear regression (MLR) technique. SOA is then estimated from the difference between the total OA and POA+BBOA masses. A similar multi-linear regression analysis is also performed on the CO data to determine the urban and biomass burning components. We also apply the more sophisticated Positive Matrix Factorization (PMF) technique to deconvolve the AMS mass spectra into hydrocarbon-like organic aerosol (HOA), biomass burning-like organic aerosol (BBOA), and oxygenated organic aerosol (OOA). A comparison of the estimates of POA, BBOA, and SOA from the MLR and PMF analyses will be presented. The $\Delta[\text{POA}]/\Delta[\text{CO}]_{\text{urban}}$ and $\Delta[\text{BBOA}]/\Delta[\text{CO}]_{\text{fire}}$ ratios estimated from both the techniques will also be compared with those obtained from the available emissions inventory for the Mexico City area as well as with the available values in literature.